Computer Simulation

Modelling of Polymer Ageing

An object oriented program is developed implementing new mathematical concepts for modelling polymer scission processes with the aid of computer interface strategies that enable easy and enhanced simulation of temporal molecular weight distribution curves of ageing polymer to explain decay behaviour observed from size exclusion chromatography at the macromolecular level (cellulose - a commercially important polymer was used for this study)

by

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Abstract

Detailed information of the underlying mechanisms of macromolecular disintegration processes is not always fully available from lab-based experiments and GPC. A powerful computer simulation technique was thus indispensable in this respect whilst saving time, labour and expense. This project aims to develop an interactive computer program to capture the behaviour of a complex reactor and offer the following functionality: mathematical calculations, graph/chart generation, processing simulation-experiment pertaining to user-given scission and environmental characteristics, data saving and re-loading etc.

Windows-style menu-driven interfaces provide templates for easy implementation of complex mathematical algorithms - a new simulation technique (Slider interfaces) presented in the thesis, based on cellulose-ageing study in electrical transformers (Heywood, 2000).

A novel statistical concept was introduced to significantly improve real-time performance of mathematical calculations to simulate polymer chain fragmentation phenomena, enabling transformation of the simple iterative to a semi-iterative and instant calculation algorithm. Three new mathematical functions were constructed - (a) Monte Carlo Dynamic (Slider), (b) Algebraic Exact, (c) Markov Statistical models, initially using an arbitrary time scale for degradation. Real-time simulation was developed using three time model variants that included the interpretation of deviations in the 1st order reaction rate from linearity to an exponential type function. The above transformation enhanced reproducibility and accuracy of degraded MWD curve sampling whilst their graphical display & clarity via ‘Cubic B-Spline’ smoothing-algorithm. Complex models were created from a ranking ensemble of single scission mechanisms, structured with levels of probability constructs to effectively simulate GPC-like curve-deformities and side-shifts.

The simulation results provided new information in the following key areas:

- the temporal shift patterns of MWD/PCLD under different ageing conditions
- graphical comparisons between simulated and observed kinetic and scission parameters.
- the dominant types of scission strategy at different reactor conditions,
- the dependence of reaction behaviour on the polymer structural order.
- An alternative way of predicting life expectancy of an ageing polymer via relating time-temperature to the magnitude of intermediate MWD curve shifts that is independent on DP. The latter is an average value and subjected to errors. An equation was derived for this.
- Introduction of a binary tree “death time” algorithm for calculation of the life expectancy of different categories of polymer chain species.

Non-iterative techniques developed here opens up new avenues of further research. The developed algorithms and computer program may provide ample scope for investigating the ageing of other industrially important polymers and can be utilised in other areas of polymer research with little modification where probability distribution is sought.
Dedication

This thesis is dedicated to my late beloved father, Dr. Shudhirindra Nath Bose, who died on 26th December 1996. I hope that, by completing this piece of research, something my father would have wished most will make him proud in heaven. My father devoted his life as a medical professional not only to serving the critically ill but also to helping poor, needy and helpless people in society. He would have liked me to continue with the same pursuit, benefiting humanity.
Preface
This Thesis includes 8 chapters in total:
Chapter 2 contains mainly a literature review of polymer degradation chemistry, background on the programming techniques used and various probability constructs used in the mathematical modelling. Chapter 3 discusses the methods developed to optimise MWD curve simulation and enhancement of simple scission models by incorporating probability functions. Chapter 4 describes the structured program design, design and implementation of various interfaces, the vital role played by the latter in obtaining desired simulation results and optimisation of models, and the implementation of various programming strategies in independent simulation studies. Chapter 5 presents the mathematical modelling methods newly devised and developed in this project with a view to further enhance the simulation of complex degradation process of linear chain macromolecules (e.g. cellulose). A new concept of formulating the statistical outcome of chain fragmentation process by means of algebraic equations is introduced through the development of mathematical algorithms replacing slow iterative calculation to an instant one. To this effect Markov chain processes are introduced to optimise the simulation of bond scission mechanisms. Chapter 6 presents all the results obtained from simulation models and compares them with those from accelerated lab-tests. A time-temperature relationship is developed to better describe the temperature dependent scission processes for cellulose including the prediction of its life expectancy. Chapter 7 introduces the concepts of different time distribution models in order to simulate real time degradation. This also introduces a binary tree molecular death algorithm and describes the kinetic results obtained from simulation. Chapter 8 then summarises the final achievements of the current project and their application to the study of cellulose, with comments for future projects.

This project study however does not concern the subject areas of the practical development of laboratory chromatographic methods such as GPC. The software simulation program is not intended to substitute the GPC
software for reproducing the MWD chromatograms or other graphic results derived from accelerated laboratory tests. The thesis presents an independent simulation study and experimentation results achieved from the developed software program, using it as the only tool. The fundamental principles of the models are purely based on hypothetical (but realistic) molecular chain scission mechanisms and their probable outcomes. The accelerated laboratory tests are used only to provide the initial molecular weight distribution of the intact polymer (cellulose) and to make a comparative study in combination with the present simulation results. The strategy is intended to afford a detailed understanding of the complex chemical molecular events in polymer degradation phenomena. A CD is also included containing an execution file of the program, with a guide lines for recommended instruction for navigation (contained in appendix 4) and three more appendices (i.e. Appendix 5, 6 and 7) containing more details as referenced in the thesis Chapters 4, 5, 6, 7 respectively.

The thesis is illustrated with a large number of diagrams, graphs and tables within the allowed limit to provide clarity and assist the reader. Mathematics provides the backbone for the modelling of a physical or chemical phenomenon, yet I believe a live physical system cannot be fully clothed in algebra. During my early study of pure mathematics, I realised that despite its very abstract nature, it helps enormously in the logical understanding of a complex system. However it may also impose a barrier to imaginative exploration. In this project, I endeavoured to overcome this barrier by introducing a computer-aided visual interpretation of a physical system. I assimilated those mathematical concepts necessary for logically understanding the relevant chemical processes and used the layers of computer-aided objects to finally harness the live functions of the chemistry into a more easily manœuvreable virtual end product. I hope that this demonstration may encourage and direct other research students to think imaginatively as well as logically while developing their own models.

Sonia Bose
Guildford Winter 2002
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Abbreviations used in the thesis chapters

BMP : Bitmap format
CPU : Computer processor unit
DNA : Deoxy-ribonucleic acid
DP : Degree of polymerisation
GIF : Graphics interchange format
GPC : Gel permeation chromatography
HMW : High molecular weight
HPLC : High performance liquid chromatography
LHS : Left hand side
LMW : Low molecular weight
MC: Monte Carlo
MMW : Medium molecular weight
Mₐ : Number average molecular weight
MW : Molecular weight
M₇ : Weight average molecular weight
MWD : Molecular weight distribution
MWS : Molecular weight scale
NMR : Nuclear Magnetic resonance
OOP : Object oriented programming
P : probability
PCLD : Polymer chain length distribution
PDCycles : Polymer degradation cycles
PDF : Probability density functions
PMWD : Polymer molecular weight distribution
PVC : Poly-vinyl chloride
Q : Polycdispersity
RGB : Red green blue (colour reference macro)
RHS : Right hand side
RNA : Ribonucleic acid
SEC : Size exclusion chromatography
W : Weight
XMW-axis : Molecular weight scale along X-axis
θ : Dispersion
σ : Variance
Electrical transformer windings wrapped with cellulose insulation in good condition

Winding removed from a failed transformer- note the degraded dark areas and the top hole where the winding has burnt out
Chapter 1: Introduction

1.1. Overview

Polymers are very important part and parcels of our everyday life. They are composed of long chain macromolecules of different sizes combined together into aggregates in a partially ordered pattern to create layers of strong structural assemblies composing a macromolecular architecture. Building these macro-structures involves primary to tertiary levels of composition and complex folding of these different components into a unique compact configuration. Thus inherent properties of polymers are very different and extremely complex compared to those of small molecules. The process of creating such a hierarchy of super molecular assembly is called polymerisation and the opposite process is depolymerisation, when the macro-structure starts to break down i.e. being subjected to attack by various degrading agents such as radicals, thermal, hydrolytic, deleterious radiation from the electro magnetic spectrum. Polymerisation is a complex process but more simplistic and orderly than depolymerisation, which may be a more chaotic, complex and time dependent process. The determination of the progress of the latter is thus difficult and uncertain. Molecular and radioactive disintegration processes are usually very unpredictable and of random nature. However, slow decomposition of macromolecules may not be a fully random process. Inherent in their macro-structure are levels of orderly organisation of well structured macro-aggregates created through various strong cohesive forces and hydrogen bonding that may enforce in turn moderately predictable breakdown stages. Thus, there emerge breakdown patterns that are characteristic of different categories of polymers. The largest aggregates disintegrate to smaller building blocks through the intermediate transient components and the molecular decomposition becomes progressively more random. Improving our knowledge of the internal chemical and physical processes occurring at the molecular level will help to improve our methods of control.
The record of temporal MWD change can be obtained from size exclusion chromatography (SEC) or gel-permeation chromatography (GPC) and accelerated, laboratory based experiments of polymer-ageing. This yields various mean and averaging attributes and moments of polymerisation, but requires more detailed analysis to decipher the intermediate molecular decay states of the polymer. The study of decomposition patterns unique to different polymer systems can proceed in three main ways – experimental observation, analytical theory or computer simulation. Experimental observations are essential, but are limited in providing only certain macroscopic information and are time-demanding and costly pursuits. Theoretical models can be formulated from analytic theories and the observed behaviour and aim to extract details of the micro-events from the macroscopic properties measured experimentally. The analytical formulations on their own are often not efficient enough to present or include all the essential features of an actual phenomenon and thus risk importing errors in their approximation of the analogy. Computer simulations offer an intermediate solution to resolving complicated problems by modelling changes in chemical and physical molecular properties. Thus building an important bridge between experimental observation and analytical deductions and providing extra capacity to emulate more system related details that could be otherwise acquired. Furthermore, computer simulation allows the testing of existing theories and a comparison with experimental observations.

Particularly in the field of polymer degradation there is a definite need of a versatile robust computer simulation program that could be used conveniently to carry out simulation experiments in a user-friendly fashion and facilitate simulation of degradation trends of any polymer system. This project is devoted to the development of such a computer software program. The program is designed with provision of a range of Windows style interfaces and dialogue boxes for inputting the values of a wide range of parameters and scission attributes to enable a simulation experiment to mimic a real system. The appropriate interfaces can be selected from the
mainframe window menus, with graphical or chart display of input data and with a selection of further tasks that can be performed prior to or during the experimental run. The program algorithm is designed to allow multiple window views of a number of simulation experiment results in order to make productive comparisons. The thesis will show a novel way of computer simulation where implementation of a variety of different mathematical models through computer interface strategies has made simulation of complex system much easier.

Many statistical models to simulate degradation are available in the literature, however most of them are applicable to a mono-disperse polymer system in order to avoid solving the complex series of equations required to allow their expansion to a poly-disperse system. Introducing levels of probability-governed design with the aid of computer interfaces can overcome these difficulties, but forces the mathematical formulation to become more and more cumbersome. This leads to a change from Monte Carlo iterative modelling to the development of a new concept of direct or instant mathematical modelling of MWD temporal curves. It will be shown that this can enhance the modelling of complex systems, generate more detailed features of MWD curves and cut down computer processing time.

A simple iterative method is transformed initially into a semi-iterative algebraic algorithm that employs the induction method, which is expanded to an instant calculation by employing a geometric progression method called 'Delta correction' and is finally extended further by the use of Markov transition probability matrices. This will demonstrate the scope for sequential advancement of mathematical modelling with computer-aided strategies enabling their practical application to the simulation of a live system. Furthermore, the simulation results can be shown to be equally reliable to discern predictable information.

Previous theoretical investigations have showed that polymer chain fragmentation processes encapsulated in mathematical expressions via simple arithmetic summations and deductions to represent newly generated
entities. Expansion of this concept will be described in the thesis that envelope the entire stepwise disintegration process of macromolecular assemblies in a polynomial relationship of decay probability terms for different molecular categories for each sequence of subsequent time-slices. The essential features of the resultant intermediate MWDs can reveal micro- and macro-scopic molecular scission details that could not be revealed from lab-based experiments alone.

1.2. Aims of The Thesis

The main objective of the project is to develop a computer model to simulate degradation of linear polymers with particular emphasis on Cellulose materials and simpler polysaccharide macromolecules. The studentship is supported as a CASE study by the National Grid Company, who is interested in the degradation of cellulose insulating paper in electrical transformers, where the life expectancy of the paper limits the ultimate life of the transformer.

The present work thus involves the following development phases:

Phase I => Design and development of a computer software program for large-scale simulation experimentation based on a prototype written by Dr. Alan Emsley.

Phase II => Development of degradation simulation models and algorithms of bond scission mechanisms based on cellulose polysaccharide chemistry; development of new techniques using mathematics and computer program manipulation; extension of the simple random models composed by Dr. Alan Emsley to Monte Carlo iterative simulation methods.

Phase III => Finally to make comparative studies between lab-experimental GPC results (of cellulose) and MWD (molecular weight distribution) graph
plots generated by these various simulation models. This involves qualitative and quantitative comparison using statistics.

The current simulation investigation will compare the effects of the developed models to those obtained from a recent laboratory based experimental studies on the kinetics of cellulose degradation carried out by Dr. Alan Emsley and his research team (Dr. Richard Heywood and Dr. Xingyu Xiao). They derived a new kinetic model that describes the degradation of cellulose in accelerated tests that simulated an electrical transformer system. They also used gel permeation chromatography (GPC) to generate MWD graphic plots of various degraded cellulose samples, but were not able to analyse the results at the molecular level. The aim would be to reproduce the GPC results and to supplement them with the extra information available from the computer models.
Chapter 2

Polymer Degradation and Structural Aspects

2.1. Introduction

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2.5. Conclusions
2.1 Introduction

Polymers are at the heart of modern technology. Polymer molecules are large compared to most hydrocarbon molecules and as such are very different in physical and chemical properties and are frequently referred to as macromolecules. A polymer is a substance composed of a number of building blocks characterised by multiple repetitive units (called monomers) and their existence and immense value in everyday life was not realised until the 1930's. Ostwald (1917) described polymers as 'the land of neglected dimensions' referring to the incredible differences in sizes between ordinary molecular and macroscopic structures within colloidal particles. The applications of these large molecular weight compounds in modern technology have proliferated for use in food, clothing, shelter, transportation, communication and medicine. Elements that constitute our body and intellect- e.g. the muscles, genes, enzymes, neurotransmitters, chromosome, immune system are all now recognised as macromolecules. Yet it was only 85 years ago that Hermann Staudinger in 1920 gave a major lecture devoted to his work and the evidence in favour of the macromolecular concept and methods of synthesis (Staudinger, 1920, 1935). As their properties were found to be so different from ordinary compounds, owing to their larger dimension, polymers were imagined to possess 'anomalous' properties.

Polymer properties depend on chain dimensions and the shape of their higher-level aggregates. The constituent chain lengths are characterised by their individual degree of polymerisation or DP, the average number of constituent monomer units. Two principal techniques of polymerisation were established by Flory (1953) and Carothers (Mark, 1940). One is condensation or stepwise reaction and the other is addition or chain reaction polymerisation. The former is activated in polymer chain formation via reaction between two polyfunctional molecules with elimination of a small molecule such as water the latter is triggered by a free radical initiator. The process of polymer degradation or depolymerisation breaks down the giant
molecule and reduces its molecular weight and the process is accelerated by a variety of environmental agents. Biodegradation, as seen in rotting of wood, cloths, deterioration of meat, burning of woods is an example of irreversible catastrophic changes in bio-materials. Some industrial synthetic polymers are designed in such a way as to make them less susceptible to deterioration by natural elements like oxygen, ozone or macro-compounds such as enzymes. However, highly reactive micro-catalysts and radicals such as hydrogen peroxide, hydrogen, hydroxyl radicals, metallic impurities, UV radiation, degrade most polymers to some extent and create problems for long-term use. Some examples of degradation are sensitivity of polyolefines to photo-oxidation (Gugumus, 1993, 1994), oxyluminescence of polyamides (Tacharkhtchi et al., 1994), photochemical decomposition of pigmented polymers such as nylon (Allen, 1993).

The processes of 'ageing' or 'weathering' of polymers range from low temperature deterioration to shear mechanical mixing through to very high temperature phenomena, such as flammability, and ablative processes. Their chemistry and physics are currently under intensive investigations in order to understand structural changes (Lehrle et al., 1995; Grimbley and Lehrle, 1995; Sakata et al., 1995; Guita, 1986; McCoy et al., 1994, 1997; Madras et al., 1995, 1996; Simon, 1992a, 1992b). On occasions, deteriorating chemical treatments are used for modification of polymer matrix composition or for creating novel co-polymers (Caeter and Goethals, 1995). Polymer properties can be designed and controlled to suit the commercial usage (Lee et al., 1996, Miller, 1994, Tobita, 1995b, 1996a, Broadbelt et al., 1995; Huang et al., 1995, Tzoganakis et al., 1988a, b). A variety of spectroscopic and chromatographic methods (Lehrle and Atkinson, 1994; Flynn and Florin, 1985) have been exploited in experimental studies of ageing. Polymer molecular weight distributions (MWD) have the potential to provide the clearest indicators of microscopic behaviour (Broadbelt et al., 1995, McCoy and Madras, 1997, Dong and Yan, 1997; Szymanski, 1998a, b). The development of Size exclusion chromatography (SEC) made it possible to capture the progressive changes in MWD as a polymer ages (Miller et al., 1991; Florea, 1993; Boryniec et al., 1997, Naga
Various theoretical models of MWD change have been developed, but are often very cumbersome and need a lot of simplifying assumptions and approximations (Romantsova et al., 1978; Aris and Gavalas, 1966; Tzoganakis et al., 1988a, b; Ranzi et al., 1997, Pladis and Kiparissides, 1998). However, computer simulation has broadened the scope for modelling polymer behaviour (Radiotis and Brown, 1997) and has the power to bridge the gap between the experimental findings and hypothetical postulations. The current work develops a computer program to use mathematical modelling methods to model degradation phenomena and simulate MWD changes during ageing of linear polymers.

The aim of this chapter is to provide some understanding of the field of linear polymer degradation processes and the issues involved. Important definitions are made to introduce the statistical and other attributes that are required to define and model the degradation characteristics. General decay behaviour of linear and other polymers is described first. This is followed by a more detailed account of degradation and decay chemistry of natural biopolymer, using cellulose as an example. Cellulose, classified as a linear polysaccharide, has been chosen for this modelling study as a representative of linear polymers for its extreme industrial importance and numerous experimental studies devoted to predicting its complex structure and kinetic behaviour. Also because MWD vs. time data were readily available from recent experimental studies. A brief account is given of the degradative behaviour of cellulose in the electrical industry. The dependence of depolymerisation characteristics of macromolecules on their structural complexity is demonstrated and a few other similar polysaccharide macromolecules are briefly compared to cellulose. The chain rupture concepts, introduced in these sections, are used in later chapters for the modelling work.
2.2. Reactions of Polymers

2.2.1. Essence of Macromolecular Synthesis (Fig. 2.1-2.3)

Reaction kinetics in solid polymers display some complex features that distinguish them from kinetics of low-molecular weight compounds, due to their heterogeneous molecular assembly, phase state and limited mobility of the polymer (Emanuel and Buchachenko, 1982). How complex is the formation of structural assemblies that finally converge to create a heterogeneous multidimensional entity is depicted in the diagram Fig. 2.1a (exemplifying biosynthesis of polysaccharides). The diagram endeavours to provide a general view to most of the polymer structure forming steps. Variable sized chains come together to form semi-ordered, inter-linked aggregates, which build into a complex, 3-dimensional, semi-crystalline structure. Dense packing of layers of polymer matrix is bound together by a network of intermolecular non-covalent linkages (Cowie, 1996). Cross-linking and chain branching propagate in an uncontrolled fashion during manufacture or growth (Tobita, 1988, 1993a-1996a, 1993b-1996b, 1993c-1996c). The formation of the cross-linked network in polymers such as vinyl and divinyl co-polymer, vinyl acetate etc. generates different properties depending whether the linkages form pre- or post-gelation.

Randomness in some synthetic processes makes it necessary to apply simplifications in order to model synthetic reactions. Existing statistical theories (Flory, 1941; Stockmayer, 1944; Gordon, 1975; Tiemersma-Thoone et al., 1991) have been used to attempt to model the composition of polymers with definable kinetic parameters (Tobita, 1995a, 1995b, 1996a, 1996b, 1996c). These modelling studies used a stochastic Monte Carlo dynamic method that describes the reactor operations as history-dependent non-random processes to relate chemical kinetics to evolved molecular constitution. It is quite far-fetched to expect theoretical models to ideally capture all the intrinsic physical complexity associated with the real system. Yet an effective model can deduce quite detailed structural information and
Fig. 2.1a-b: (a) diagram shows complex levels of structural architecture, (b) importance of MWD in providing with statistical information of the state of integrity of this architecture, specially in the case of polydisperse polymer.
spatial chain density distribution in some systems, which is necessary to optimise the functions of many industrial synthetic or man-made polymers by means of reconstructing their compositions. A number of such current researches as exemplified above have been devoted to furnish such individual commercial need (Miller, 1994; Krol, 1995; Lee et al., 1997; Ha and Chu, 1997; Kremsel et al., 1997; Szymanski, 1998; Kim and Soares, 1998), devising new models either via lab-experimentation or simulation.

There are varieties of instrumental methods for deriving molecular structural information but with very limited provisions. The recent development and popularity of GPC method proves to be the only ideal solution in the case of clear resolution of polymer structural changes. The latter is given in the form of a statistical distribution of the concentrations of the different species comprising the entire matrix. The resultant chromatogram provides MWD of the entire polymer macromolecule or chain species, which is used to provide information regarding the individual states of the latter. This fingerprinting of polymer building blocks (Fig. 2.1b) is analogous to fingerprinting of amino-acid building blocks of peptides (the secondary structural components of protein) by HPLC and sequencing of DNA or RNA fragments (the secondary building blocks of genetic materials) by Gel Electrophoresis.

### 2.2.2. Essence of Macromolecular Degradation

The processes of degradation are also random, but can be imagined to be more chaotic than polymerisation, as a series of "polychromatic" kinetic processes that promulgate from a spectrum of possible reactions. The latter are postulated as the "neighbouring" effects, configurational and conformational effects, steric hindrance effects, limiting permeability effects, effects arising from differential aggregational densities and polymer phase density and many others (Plate et al., 1977; North, 1974; Patrick, 1972). The conformational effects depend on the variety of ways two inter or intra-molecular reactive moieties can come into contact within an allowable distance for an inter- or intra-molecular reaction to proceed. Probability for
this to happen and the rate of reaction depends on the probability of the conformation relating to the realisation of the transition complex as well as on the lifetime of this favourable conformation. Furthermore, any such conformational change in a given section of a macromolecule may favour or upset the course of subsequent reactions that occur with the participation of neighbouring functional groups (Flynn and Florin, 1985). Thus specificity of particular macromolecular reactions is developed through a cascade of conformational re-arrangements associated with corresponding changes in the nature of the subsequent course of reaction. As a result, assemblies of units of the same type joined by the same chemical bonds in a macromolecular system often behave differently from a collection of small molecules with similar chemical structures (Plate et al., 1977; Emanuel and Buchachenko, 1982). Thus different categories of reaction strategies need to be conceptualised for different parts of the matrix, when a polymer is considered as a whole.

There are other effects to consider: –

- Supra-molecular structure and physical structures (fibrillar, spheroidal, semi-crystalline) in solid polymers hinder reaction progress, due to non-uniformity of reagent distribution and pore permeability (Popov et al., 1987, Enikolopian et al., 1982, 1984, 1987).
- Differing morphologies of a polymer exhibit differences in kinetics and mechanisms of reaction.
- Radical impurities initiate oxidative ageing of solid polymers such as polyolefins, polyamides and polydiene elastomers.
- Properties such as tensile strength and permeability are shown to be remarkably dependent on the stretches of the “tie” connections between neighbouring crystallites. Increase in structural imperfection has been demonstrated to make polymers less thermostable and less ductile (Tanaka K. et al., 1993; Tanaka A. et al., 1973; Belveoch and Gueneir, 1959; Perena et al., 1982; Miyaji and Assai, 1978).
- Some non-crystallisable polymers exhibit an unusually tough elastomeric property. Ductility of their intermolecular network depends on
the polydisperse chain length distribution, and inter-connectivity between short and long chains (Tobita, 1998; Zaichenko et al., 1998; Sharaf and Mark, 1993, 1994; Andrady et al., 1980; Mark, 1982; Falender et al., 1979).

2.2.3. Parallel and Competing Processes

Thermal depolymerisation or pyrolysis is a key method of studying chemical and physical processes during ageing of polymers (Sakata et al, 1995, Madras et al., 1995, 1996a, b; Ranzi et al., 1997). Grimbley and Lehrle (1995, 1996) examined decomposition characteristics of a number of synthetic polymers such as polymethylacrylate, polyisobutylene, polystyrene and bio-polymers such as natural rubber and BIOPOL (bacterial poly(hydroxybutyric acid)). They used a high temperature range (400-500°C) to study the nature of molecular processes during both complete and partial pyrolysis (Lehrle et al., 1996, 1995, 1994). The major decomposition products were found to be monomers and lower oligomers. Their analysis suggested the existence of at least three different parallel competing reactions with a possibility of a fourth. They proposed random scission, depopagation or unzipping into monomers, intermolecular chain transfer during unzip and a minor secondary recombination reaction of the primary products. The initial thermal decomposition proceeded with a high percentage of random scission mechanism but was soon superseded by the others. However, the scission pattern was observed to change in partial decomposition, where a kinetically favoured end-scission prevailed with a favourable yield of oligomeric products. Guita in 1986 and then together with Chiantore in 1990 and 1993 have also observed difference in combination of competing reaction processes in studying thermo-decomposition of polystyrene below and above 300°C in the absence of oxygen. Below 300°C, an autocatalytic oxidation occurred, where depolymerisation did not yield any of the lower oligomers observed at higher temperatures. The competing processes were characterised as depolymerisation or unzipping and intra- or intermolecular chain transfer. A combination of the latter processes was thought responsible for recombination of the residual low
molecular weight fragments, yielding a wide range of oligomeric products. A preferential cleavage of thermo-labile weaklinks (Chiantore and Guita, 1993; Jellinek, 1948a, 1948b, 1955; Grassie and Kerr, 1959; Cameron and Kerr, 1968, 1970) was thought to be responsible for the deviation from the linearity of the predicted first order kinetics.

The above examples demonstrated that preferential switches in reaction modes, together with sustained parallel chain scission mechanisms, cause deviations from kinetic uniformity. A number of researchers have identified similar observations of a cluster of competing reactions and a concomitant departure to non-linearity (Chan and Balke, 1997; Nguyen, 1994; Simon, 1992a, 1992b; Miller et al., 1991).

2.3. Modes of Degradation

2.3.1. Degradative Agents

Organic molecules or macromolecules, composed of carbon, hydrogen, oxygen and nitrogen, are comparatively less heat resistant than inorganic materials and are thermo-stable only below a limiting temperature range normally 100-200°C (Madorsky, 1964) and readily decompose into small fragments such as free radicals, free ions, H₂, CO, etc. Dissociation energies of a single covalent bond in the ground state are in the order of 150-400KJ per mol at 25°C (typical values: O-O: 147; C-H: 320-420; C-C: 260-400; C-O: 330 KJ/mol). A covalent bond is hard to break at ambient temperature thermal energy (average value of kT = 2.4kJ/mol) in the absence of alternative activating agent and generally requires a temperature elevation of a couple of hundred degrees (Reich and Stivala, 1971). However, in condensed systems, rapid dissipation of vibrational energy distribution among molecules and bonds might prompt a certain fraction to vibrate with significantly higher energy-state than average. This fraction of excited bonds increases with increasing temperature, reaching the energy quota for repulsion when a bond rupture occurs. In effect, a sufficient rise in
temperature aids in the absorption of adequate energy quanta to enable the
dissociation energy to be exceeded, promoting significant degradative
transition (Lum, 1981; O'Mara, 1970; Faroq et al., 1994; Wang et al.,
1995). Hence at comparatively lower temperatures (100-300°C) patterns of
bond scissions reactions include only those with lower activation energies,
whereas those with high thermodynamic demand can only be broken with
increase in temperature (Liebman and Levy, 1985; Grimbley and Lehrle,
1995; Lehrle et al., 1996). Changes in polymer degradation mechanisms,
variation of chain length participation in van der Waals interaction and effect
of thermal history on kinetic parameters have been critically analysed,
comparing isothermal profiles with temperature programming conditions
(Flynn, 1978a, 1978b, 1981; Dickens and Flynn, 1983; Wittkop et al., 1996;
Chan and Balke, 1997; Aris and Gavalas, 1966).

Chemical degradation reactions (e.g. oxidation, radical chain mechanisms)
can be accelerated with a small temperature elevation (150-300°C) from
ambient (Madras et al., 1996a, 1996b, 1995; Gugumus, 1993, 1994) and are
generally temperature dependent (Schnabel, 1981). It is frequently found
that the presence of impurities or additives in a polymeric matrix induces
high reactivity similar to that occurring at high temperatures. This shows
there is not much significant difference between low-thermal or thermo-
chemical mode of initiation.

Other modes of degradation can take place under low or ambient
temperatures such as biological, mechanical, light, photo or radiation
induced attack on polymers (Allen, 1983, 1994; Mwila et al., 1994;
Muzzarelli, 1978; Damszy and Roberts, 1992; Muzzarelli and Rochetti,
There are a great variety of enzyme macromolecular biocatalysts produced
from biological or microbial sources. Each is capable of reacting with both
natural and synthetic polymers in a wide range of low temperatures – the
highest optimum normally being 60-70°C (Gopferich and Langer, 1995;
Greizerstein et al., 1993; Chasin and Langer, 1990; Lenz, 1993; Leenslang
et al., 1987; Heller et al., 1990; Li and Kohn, 1989; Pistner et al., 1993).
Enzymes are very susceptible to high temperatures and rapidly lose their active form. Enzymic attacks on polymer chains are seldom random in nature and rather are quite specific with respect to bond locations, determined by the conformation of the enzyme macromolecules. Usually, reaction comes to completion faster than other modes, with zero order kinetics. Similarly, stress induced processes, e.g. mechanically initiated degradation under the influence of shear forces, bring about macroscopic physical fracture along the polymer backbone and are another example of a non-random and temperature unaided process (Nguyen, 1994; Thomas, 1959; Van Der Hoff and Gall, 1977; Price and Smith, 1993). Centre portions of the polymer main chains are more susceptible to rupture. The application of such mechano-chemical inductive process plays an important role in synthesis of block and graft copolymers.

When structural decay occurs via irradiation of polymers with ultraviolet or visible light, processes can be random and bond rupture tends to progress equally throughout the whole body of a polymer matrix. The result may lead to severe property deterioration. The existence of chromophoric groups in the macromolecules or additives is a prerequisite for photochemical reactions to occur. Other similar processes with much higher energy radiation such as electromagnetic (X-rays, γ-rays) or particle (α-rays, fast electrons, neutrons, nuclear fission products) radiation does not require the existence of chromophores and is driven by a molecular interaction with the radiation. The extent of chemical and physical change is characteristic of the chemical composition of the material and on the nature of the radiation. This means of modifying polymeric materials is common in fields of high radiation flux (e.g. nuclear reactors) due to generation of reactive intermediates (free radicals and ions) in the substrate (Schnabel, 1981).

In a real system, various modes of degradation often occur simultaneously, making the reactor processes more complicated to define as the processes compete with each other and yield a complex undefined rate constant from the outset. Hence the conversion rate often deviates from any definable
order to an indeterminate state. Slow decomposition of cellulose insulation in an electrical transformer is an example to the above (Emsley 1994a, b; Emsley and Stevens, 1994a, b; Emsley and Heywood, 1995, 2000; Ali et al., 1996). A range of events can therefore evolve in a series of chemical reactions, which are generally either radical or ionic reactions following either a single stepwise reaction or a chain mechanism (Schnabel, 1981).

2.3.2. Effects of Degrading Agents

Oxidative: A large number of synthetic polymers of industrial importance degrade rapidly via catalytic oxidation that requires the presence of oxygen and high temperatures or micro-catalyst compounds such as transition metals or additives. Oxidative or autocatalytic degradation, aided by thermal or incident photon energy, is the most widespread cause of polymer failure in terms of loss of mechanical strength, durability and resistivity (Rabek, 1975; Reich and Stivala, 1969). Polymer oxidation reactions or radical scission mechanisms usually progress in three main stages. From initiation steps forming radicals through propagation of the latter or chain reactions (C-C bond cleavage by beta scission) yielding smaller molecular weight products to a kind of termination reaction (via recombination, disproportionation or hydrogen abstraction), which neutralises the radicals. At the initiation stage, low molecular weight active radicals are formed. Radical chains propagate as micro-radicals diffuse through the polymer matrix at random to various sites yielding reactive high molecular weight or macro-radicals. The latter species are generated from the collision of highly reactive micro-radicals with comparatively inactive long polymer molecular species. A range of more reactive radical species (macro-radicals) of differing molecular sizes (e.g. high molecular weight peroxide radicals) are involved in polymer chain scission. The termination stage produces inactive products or decay of radicals via a number of pathways. The kinetics of radical chain reactions is complex and difficult to determine, as is the rate-controlling factor.
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Thermo-oxidative: Polyolefins are thermodynamically unstable to the environment, resulting in a slow degradation into carbon dioxide and water even at ambient temperatures (Henry et al., 1992). Barr-kumarakulasinghe (1994) has reported a life-prediction model based on a simple kinetic equation due to Guryanova et al. (1967). Degradation kinetics were calculated in terms of experimentally established rates of initiation of peroxy radicals, regarded as the rate limiting step, and transformed into a life-prediction model, which related the variation of percent elongation of oven aged polymer films with time. Half-life prediction curves at various temperatures were used to establish the analytical model, which relies on solving a range of kinetic equations involving manifold parameters. This is an example of linking mechanical properties to chemical kinetics, where experimental measurement of the chain elongation criteria was required to solve the model equations. This model could have been simplified if structured using a Monte Carlo method and independently simulating the dependence of physical elongation characteristics on the rate of the chemical initiation process.

Thermal: Thermal degradation or pyrolysis usually gives rise to radically initiated scission mechanisms, which may lead to chain-end depolymerisation with unzipping and leave different zip-length fragments behind. This may be driven by auto-oxidative (e.g. polyolefins-polypropylene, polystyrene) or non-oxidative (e.g. cellulose) mechanisms. Normally the formation of critical radical concentration is the rate-determining step (stationary state), the overall degradation rate precedes first order in the polymer concentration (Madras et al., 1996 a, b).

Hydrolytic: Polysaccharide glycosidic linkages are susceptible to acid catalysed hydrolysis yielding simple sugar monosaccharides. The kinetics of this phenomenon has been widely investigated under various conditions and substrates (Nevell, 1996, Hjerde et al., 1999). Micro-structural identification of important complex bio-molecules such as proteins, nucleic acids, polysaccharides have used controlled hydrolysis since the 1920s. The
process of hydrolysis is also exploited for manufacture of many modern commodities incorporating hydrolysable linkages. These include polyesters, polyamides, polyurethanes, poly(dialkyl siloxanes) and polycarbonates. Hydrolysis mostly acts on the main chain structure cleaving the most susceptible linkages (Stokke and Christensen, 1996; Hjerde et al., 1999, 1998a, b; Basedow et al., 1978) and can create centres for subsequent thermal degradation. Due to the structurally inherent hydrophobic nature of most organic macromolecules, hydrolysable linkages are usually hidden underneath the exposed surfaces and as a consequence restricted access to the interior reduces the speed of the process. Thus crystalline regions of a polymer are less susceptible than amorphous regions. Hydrolysis may compete with thermal degradation at high temperature in some polymers such as poly(ethylene terephthalate) and polyamides where traces of moisture are trapped or evolved as by-products of previous reactions (Ravens and Sisley, 1964; Gesner, 1972).

2.3.3. Chain Rupture

Chain cleaving mechanisms can occur in a number of ways, such as in general at random points along the chain, at the terminal end of a polymer macro-radical or towards the centrally located bonds and frequently results in unzipping of a random number of monomer units. Thus chain depolymerisation processes are the reverse of the two main types of polymerisation processes.

1) Random chain scission releases large or medium sized mixtures of fragment chains, comparable to condensation polymerisation (Tian et al., 1998; Madras et al., 1995; Lehrle et al., 1994, 1995; Grimbley and Lehrle, 1995; Huang et al., 1995).

2) Chain end unzipping or depolymerisation mostly yields a vast number of volatile or non-volatile monomer units, comparable to reverse

There are conflicting opinions with regard to whether the distribution of weak-links is random or prefixed. Some argue in favour of the former (Cameron and Kerr, 1968, 1970). Others (Jellinek, 1948a, 1948b, 1955; Grassie and Kerr, 1959; Chang and Balke, 1997) support the latter. Many interesting structural spectroscopic and electron microscopic analyses have been devoted to identifying weak-links (Bower and Maddams, 1989; Allen, 1983). They could be at branch points (Grassie and Kerr, 1959) intramolecular unsaturation (Cameron and Grassie, 1962b, Mayo and Miller, 1956), head-to-head linkages (Cameron and Grassie, 1962a) or possibly at the chain ends, chain folds or junctions. The question still remain as to whether they exist at all and, if so their frequency and concentration.

A third kind of rupture mechanism is of importance in estimating total degradation activity in the case of bio-macromolecules, where higher levels of structural and conformational changes are required to be taken into account. This may be referred to as breaking of secondary valence bonds within a chain and between chains e.g. hydrogen and van der Waals bonds. Rupture of these bonds is essential in the initial degradation invasion by any chemical agents. This degradative process is called denaturation and is influenced by heat and pH changes.

A few other mechanisms have been reported, such as central scission, carbonation, intermolecular recombination, 'back-biting', 'cage-effects' mechanisms (Flynn and Florin, 1985).

### 2.3.4. Statistical Attributes

Most polymeric materials are polydisperse i.e. containing a distribution of chain lengths. A monodisperse polymer consists of all chains of equal size and is only found in some synthetic polymers. The degree of polymerisation
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(DP_n, DP_w) and polydispersity (Q) indices together represent important measure of polymer property indicating increase or decrease in number fragments and weights. Degradation is a fragmentation phenomenon of polymer long chain molecules, and as such gives rise to an ever-changing frequency distribution of these entities called MWD or PCLD that includes both parent molecules and their newly evolved progenies. Population balance equations are often constructed to enable a straightforward means of deriving expressions from the moments of frequency distributions (McCoy and Madras, 1997). There are various mathematical treatments for quantitative assessment of degradation, but most rely on the consideration of an averaged value that may not be accurately consistent with the temporal changes. This may include calculation of average properties such as moments of chain lengths or their average DP i.e. mean of a molecular weight distribution (MWD) with time or integro-differential assumptions. A number of mathematical and statistical treatments have been reported (Montroll and Simha, 1940; Simha and Wall, 1958; Jellinek, 1955, 1978, 1983; Hamid et al., 1992). The statistical mean values of MWD's are often used to determine polymer chain decay kinetic rates and mechanisms, but the MWD itself represents a statistical chart holding more explicit information than its averaged indices. The current developed computer program is aimed to examine these characteristic deviations observed in the subsequent MWD decay-curves from their original form, in terms of simulating a network of molecular events of chain-breaking phenomena.

2.4. Cellulose as a Model for Linear Polymer

2.4.1. Cellulose Complex Structure (Fig. 2.1-2.3)

The Fig. 2.4a presents the cellulose primary structure, composed of simple repeating units of D-glucopyranose, covalently bonded together in a stable β configuration via C1-C4 glycosidic oxygen linkage, with the second glucan unit inverted relative to the first. These linear chains are intricately packed to form fibrillar micro-crystallites (Fig. 2.2 and 2.1a) interlinked in a very orderly
Fig. 2.2: Macromolecular Structural Hierarchy Formation via Chain Aggregates
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helical expanded conformation via hydrogen bonding. The fibrils are aggregated in sheet-like layers (Fig. 2.3) held together with van der Waals forces (Kennedy et al, 1998). These higher levels of structural order contribute to a complex form of semi-crystalline structure, which is largely responsible for the kinetic diversity and unpredictability of chemical reaction mechanisms of this otherwise simple linear homo-polymer. Some conclusion can be drawn with regard to the manner of chain cleavages during degradation from reaction mechanisms described later. The molecular weight or DP of cellulose differs depending on its native source and its extraction and processing treatment for commercial use. A cellulose polymer chain may consist of 1000 - 15000 glucose units depending on its origin and the extent of possible degradation during its isolation.

In the $^1C_4$ chair conformation, the CH$_2$OH and OH groups across the glycosidic bonds are equatorial with respect to the plane of the polymer backbone chain. This conformation is energetically the lowest of six conformations, adopted by a polysaccharide chain. In addition, strong hydrogen bonding (bond strength > 0.5kJ/mole) between adjacent oxygen and hydrogen atoms forces a linear arrangement and stabilises the chain structure further. The bond length and angles have been determined by X-ray diffraction methods. The latter reveals that the distance between each glycosidic oxygen atom is 0.544 nm so that a repeat distance of 1.08 nm prevails along the chain (Okumura, 1989; Emsley and Stevens, 1994a).

Structural characteristics have decisive influence on physico-mechanical properties of a polymer. In defining the structure of a fibrous polymeric substrate like cellulose, it is important to distinguish its three structural levels - molecular level, supra-molecular level and morphological level. The 3-dimentional levels of molecular organisation bring complexity and rigidity in biopolymers and may impart slower rates of decay to regions of particularly higher order. Thus the influence of variable rates of degradation in different regions will be examined in the simulation results presented in chapter 6. A brief concept of these different levels of structure is given below.
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Intermolecular or intra-molecular interactions among the polymer chains are non-covalent bonding forces between neighbouring hydrogen and oxygen atoms within the same polymer chain and between chains. They are vital for chain association and responsible for microfibril formation and tertiary arrangement of the fibrils in crystalline strands. Intramolecular hydrogen bonds are usually formed as follows (Krassig, 1985).

1. The hydrogen atom of the hydroxyl group on C(3) and the preceding Pyranose ring oxygen O(5).
2. The hydrogen atom of the hydroxyl group on C(2) and the succeeding hydroxyl group on C(6).
3. Intermolecular or interplaner hydrogen bonds - hydrogen bridges are formed
4. Hydroxyls on C(6) and hydroxyls on C(3) of the neighbouring down chain in the centre 002 plane, alternating in direction.
5. Hydroxyls on C(6) and hydroxyls on C(2) of the neighbouring up chains in the corner 002 plane.
6. Hydroxyls on C(2) and hydroxyls on C(2) from each second glucose unit of the centre “down” and the corner “up” chains between neighbouring anti-parallel chains in the 102 plane.

2.4.2. Hydrogen Bonding and Crystallinity

Cellulose biosynthesis - Cellulose is most abundant in plant cell walls as a structural polysaccharide and is the major component of wood and paper and a unique structural element in cotton. It is also found in some invertebrates (insects) as exoskeleton. Uridine Diphosphoglucose (in plant cell walls) or Guanosine Diphosphoglucose (in lower invertebrates or microorganisms), the nucleotide donors (NDP), is the precursors of glucose units taking part in the synthesis of the primary cellulose residues. These are then added to the end of an active glucan chain within the cells by an enzyme catalyst - cellulose synthase:
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NDP-glucose + [glucose]_n → NDP + [glucose]_{n+1}

The latter are then transferred to the outside of the cells through pores, where these chains associate into microfibrils (Fig. 2.2) non-enzymatically via hydrogen bonding. The hydrogen bonding within chains, maintains a linear conformation while hydrogen bonding between cellulose chains assists in fibril formation. The latter not only stabilise the two-fold screw axis or the helical structure but also impart the stiffness and rigid nature of cellulosic materials.

Supramolecular level aggregation (Fig. 2.1a) - light microscope magnification and electron microscopic study reveals the fibrillar structure of cellulose fibres - macrofibrils are aggregates of much thinner and more basic fibrillar units – microfibrils. The latter have a cross dimensions of only 3-20 nm and macrofibril dimensions vary widely in diameter between a few tenths of a micron up to several microns (Krassig, 1985). X-Ray microscopic study (Chang, 1971, 1974) reveals that cellulose is a para-crystalline material with regions of high crystallinity and amorphous regions (Hatakeyama et al., 1987). In the crystalline regions, the polymer chains adopt parallel positions in a monoclinic lattice and thus enforce resistance to initiation of chain breakage due to higher ordered rigidity. There are also regions that are less ordered – semi-crystalline (Okamura, 1989), with lesser resistance. Studies in this area indicates that hydrogen bonding together with van der Waals cohesive forces produce sheet or layered aggregates (Fig. 2.3). Thus breakdown of these forces are necessary before any further disruption can occur at the molecular level. As a result, the rate of chain rupture differs among the polymer population according to degree of order.
Fig. 2.3: Cellulose Crystallite Sub-allomorphs - Rotational changes around C6-C5 bond

Various Glucan Mini-sheet Planes
i. Left
ii. Right
2.4.3. Degradation in a Simple Reactor

Three main reaction modes are considered below as separate reactions with the most recent experimental observations.

2.4.3.1. Thermal (Fig. 2.4 a-c)

Early work on cellulose degradation in vacuo was thought to obey first order kinetics and be non-oxidative in character (Schwenker and Pascu, 1957; Stamm, 1956). The initial degradation process was believed to be a radical-driven, random process that yielded two products - a fraction of very low molecular weight reducing sugars and a fraction of very high molecular weight polysaccharides.

Decomposition below 250°C exhibited an initial induction period of low rate and rapid degradation at temperatures above 250°C. The main product reported was levoglucosan, 1,6-anhydro-β-D-glucopyranose (I). It was believed that 1,4-glucosidic bond cleavage would be a radical process where each rupture of a hemiacetal linkage yielded a water molecule (Tishchenko and Fedorishchev, 1953; Pakhomov, 1957). Compound I was found in abundance from the densely packed highly ordered crystalline regions. A large number of experimental studies during 1950-70 were dedicated to the investigation of chemical mechanisms that finally yielded levoglucosan. No definite pathway was identified owing to the complex nature of reaction processes, dependent on the temperature. Conley (1970) suggested a few key mechanisms operating in succession or combination.

Thermolytic decomposition (Fig. 2.4a-c) of the cellulose 1,4 glycosidic linkage via 1,5 hemiacetal linkages occurs with loss of water molecules. The key intermediate evolved from the former cleavage is believed to be an isomeric form of anhydro sugar unit (I) rather than glucose. Here radical chain scission is the preferred mode to hydrolysis and is associated with chain end conformational change between α and β - two isomeric forms.
Thermal Nonoxidative Degradation of Cellulose: Homolytic Cleavage
Resultant of Two Parallel Processes: Dehydration + Depolymerisation

(a) Cellulose Primary Structure: Linear chains of Anhydro-sugar units in ether linkage

(b) Chain fragmentation yielding Levoglucosan
(c) Interchain network formation
Pathways Predominant in Crystalline Regions

Fig. 2.4 a-c
accompanied with ring conversion from pyranose to furanose configurations (Fig. 2.4b). Alternatively, simultaneous dehydration and depolymerisation can occur followed by intramolecular displacement of an oxygen atom attached to C-1 of a glucosyl unit (Conley, 1970). At around a temperature 200-300°C, region structural changes are accompanied by chemical transformations and several processes compete with each other and with the formation of tar-forming precursors. Additional inter-chain etherification (Fig. 2.4c) processes between neighbouring hydroxyl groups and C-4 carbons may also take place, splitting the chain at some central location and producing a three-dimensional chain network. This transformation is believed to give a more stable ether linkage than the original acetal-ether chain-extending unit. The formation of the latter is believed to stop successive chain depolymerisation or unzipping, which is typical of other auto radical chain scissions. It has been shown that other decomposition products (e.g. 5-hydroxymethyl furfural) are formed during pyrolysis of cellulose.

2.4.3.2. Hydrolytic (Fig. 2.5 a-c)

This mode of degradation can also proceed in nonaqueous protic (Fig. 2.5a-c) and aprotic media such as dry alcohol. Ethanol or methanol initiated alcoholysis is analogous to hydrolysis, but the rates observed are higher due to less strong solvation of the H⁺ than in water. As water cannot be completely excluded from the system, it abstracts acid (Fig. 2.5a) preferentially from the protic medium to form acid-saturated water solutions that are in turn absorbed by the polysaccharide (Fig. 2.5b-c) to give high hydrolysis rates. The complete absence of a protic medium inhibits acid degradation. The only dry acid able to degrade glucosidic bonds is HF by forming unstable glucosyl fluorides, which tend to drive reverse depolymerisation giving linear and branched oligosaccharides of DP ranging between 14-18. In HCl-catalysed degradation of cellulose in (aprotic) benzene, the presence of traces of water molecules in the system play important role in providing the vehicle for extracting inorganic acids from the organic phase into aqueous solution. (Torres et al., 1985)
Instance of Heterolytic Cleavage via Formation of Carbonium Ion: Acid Hydrolysis of Cellulose

Fig. 2.5 a-c: Hydrolysis via formation of cyclic Carbonium-Oxonium ion - (a) protonation of glycoside oxygen, (b) dipole interaction induced unstable carbocation, (c) reformation of reducing hemi acetylic hydroxyl through deprotonation via adjacent water molecule.
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Hydrolysis of cellulose with water requires a high temperature in the range of 220-300°C. The rate being much slower than thermal or oxidative degradation due to structural complexity and the amount of glucose formed is very low. To get a 50% conversion or above, the temperature needs to be raised to 230°C or above. The pathway may partly follow acidic and partly alkaline reaction routes. The activation energy of degradation of cellobiose has been shown to be as high as 136.0 kJ/mol (Bobleter and Bonn, 1985), compared to 129.1 kJ/mol for cotton cellulose (in the higher temperature range 215-274°C) (Szejtli, 1976). In the lower temperature range of 0-100°C, the dissociation energy for acid hydrolysis of cellulose is 127.5 kJ/mol.

Models of the thermodynamic properties of macromolecular cellulose from combustion enthalpies show a difference of 180 kJ/kg between crystalline and the amorphous forms. This relatively large energy difference explains the stability, persistence and difficult hydrolytic reaction conditions exhibited in the crystalline cellulose. The model data predicts 69-71% crystallinity in cellulose (excluding cotton), in good agreement with experimental results (Tarchevsky and Marchenko, 1991).

2.4.3.3. Competing Scission Reactions (Fig. 2.6 a-b)

Hydrolytic cleavage processes are observed to compete with other reaction modes in thermally aided systems, in particular with dehydration reactions. The latter are initiated by two main mechanisms – free radical and ionic. The free radical reaction is thermally activated and rates of dehydration increase with temperature. At medium temperatures, in the range 200-270°C, the predominant products of dehydration are Levoglucosan, anhydropyranoses, anhydrofuranoses, pyranosonones and furanosenones. Furfurals were observed at temperature greater than 270°C, generated via additional dehydrogenation of these intermediate products (Sjostrom, 1981). Furfural may also be evolved from triple dehydration of simple sugars, produced following the acid catalysed ionic degradation, giving, in addition, formic and levulinic acids (Fengel and Wegener, 1984).
Another important side reaction that can occur is condensation, by reaction with molecules other than water to form other polymerised products. The reacting species may come from the cellulose itself or any polyoses present in the composition e.g. lignin (Moiseev et. al, 1979) or small polyosic chain fragments or sugars (Abatzoglou and Chornet, 1998).

According to Saeman (1945) dilute acid-catalysed thermal hydrolysis (Fig.2.5a-c) of cellulose is a combined phenomenon of three main interconnected reactions – the first and major step being glucoside bond hydrolysis, followed by a whole array of thermal and catalytic decomposition reactions. This situation makes it impossible to define a true kinetic model based on the precise knowledge of the entire reaction mechanism, diffusion activity and Arrhenius dependence. Models derived using simplifying assumptions are called pseudokinetic models and different sets of kinetic parameters, from statistically designed experiments can yield different results.

A Superficial postulation of Shafizadeh (1968, 1972, 1979, 1985) hypothtsised two possible routes:

1) First step in cellulose decay is most probably initiation of a scission at the covalent bonds (glycosidic linkages) along the backbone, may be driven thermally by radical (Fig. 2.4a-c) or hydrolytic (Fig. 2.5a-c) catalysis.

2) Changes to chain conformation and glucopyranose ring conformation lead to bond breaking with the yield of an intermediate (anhydro glucopyranose or Levoglucosan).

A wide variety of end products (Furan compounds Furfural - a range of alcohols, aldehydes, ketones phenols etc.) are produced from the further decomposition of these intermediates. Differing opinions are expressed with respect to the yield of the main intermediate product - Levoglucosan - whether derived from the main chain or as a secondary by-product following
main chain degradation oligomers. Evidence suggests the possibility of two kinds of fission – homolytic (Fig. 2.4a-c) depolymerisation via a free radical mechanism (Kislitsyn, 1971; Arthur, 1966) or heterolytic (Fig. 2.5a-c) scission via carbonium ion intermediates.

**Mechanism I (Fig.2.6a)**
Supported by Golova et al. (1957a, b, c) & Kislitsyn (1971) - Cleavage of the cellulose chain is initiated by -CH₂-OH attack on the glycosidic link. A further glycosidic bond rupture to yield Levoglucosan follows an end group rearrangement. This kind of chain rupture may occur at any site along the length of a chain. This mechanism may be indicative of radical or hydrolytic degradation.

**Mechanism II (Fig.2.6b)**
Supported by Gardiner (1966) & Byrne (1966), who believed that the onset of chain cleavage begins with intra-chain conformational change inducing the formation of Levoglucosan followed by chain scission. This type of rupture is suggested to be most likely to take place at the chain end sites and may be indicative of thermally initiated chain scission via conformational transformation, which may ease off the stringent hydrogen bonding ordered structure resulting in bond breakage at the chain end. Byrne (1966) and Shafizadeh (1972) postulated that it might be due to the variation in electron density of the glycosidic bonds.

Some researchers such as Golova et al.(1957a, b, c) and Shafizadeh (1979, 1985) believe that degradation proceeds via pyrolysis and initial dehydration in the regions of high crystallinity. The latter varies according to the source of native cellulose. A labelling study of Houminer and Patai (1969) showed the formation of furfural from glucose. This end product may therefore be yielded via any intermediate oligomers produced at any stages in the polymer decay pathway where 80% of furfural is formed via route A and 20% via route B.
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*Key Mechanisms for Cellulose Chain Rupture*

Fig. 2.6a-b: (a) Mechanism I, (b) Mechanism II
2.4.3.4. Summary of Chain Ruptures

The thermal mechanisms suggest two preferred methods of chain rupture at the macro level. End chain depolymerisation or unzipping giving rise to thermo-labile compounds which decompose further to other smaller multiple carbon compounds, which volatilise from the system depending on the temperature. Primary chain scission may occur anywhere along the chain, but probably, preferentially in a middle position followed by etherification at one end stopping any end zipping. However other the end can undergo unzipping, giving rise to volatile monomeric products.

The hydrolytic mechanism suggests homogenous acid catalysis proceeds by chopping away small portions from the parent molecules. This generates low molecular weight oligo-saccharides in the amorphous region while the crystalline region still remains inaccessible. If all of the glucoside bonds were equally accessible and reactive, acid-catalysed hydrolysis of the polyoses should run to completion breaking the glucosidic bonds equivocally to simple pentoses and hexoses (sugars). In reality the situation is not so simple, because of interactions within the matrix and as a result degradation may proceed via multiple type reactions leading to a non-random or preferential cleavage. In contrast hemicelluloses as a non-crystalline, highly disordered polymer easily exposed to random attack (Fengel and Wegner, 1984).

2.4.3.5. Cellulose Compared to other Polymers (Fig. 2.7-Fig. 2.9)

In the case of biopolymers, thermodynamically stable molecular conformation is perturbed by thermal destruction. Irreversible functional and structural damages may result in transition from helical to random coil form (Christension et al., 1993, 1996). The latter means dissociation of double helices into single strand polymer chains as a result of thermal or thermo-hydrolytic disruption brought about in the key conformational foundation along with the melting of hydrogen bonds and van der Waals interactive forces (Lund et al, 1990; Burton and Brant, 1983; Ford and Atkins, 1989;
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Rinaudo and Milas, 1980). Repeated invasions destroy the cooperative helical folding of the orderly or crystalline regions and make those hidden bonds more accessible to cleave (Rowland and Roberts, 1972; Hatakeyama et al, 1887; Schafer and Stevens, 1995).

There are some striking structural similarities between multistranded polysaccharides (e.g. Xanthan, Scleroglucan, Schizophylin, Pollulan etc) and cellulose (Fig.2.7a-d). The latter illustrates stronger strand formation by association of double or triple helices than single one in an analogy to two-fold single helical backbone of cellulose. A stronger intermolecular cooperative force is the key feature in multiple strand formation that imparts stronger thermal stability among these polymers through the sustenance of higher ordered helical conformation. The intricate linking of the helices protects the polymer matrix from easy attack of free radicals. Further quaternary folding of the helical aggregates envelope them into two surfaces - hydrophobicity in natural polymers is due to this strategy. The hydrophobic surface protects those hydro-labile molecular linkages from invasive hydrolytic attack. This analysis tends to regard hydrolysis as a preferential process, being restricted to invading only the amorphous layers at sites close to crystalline chain extremities. The chain species comprising the crystalline lamellae contained in hydrophobic surface remain inaccessible (Launay et al., 1994).

Examination of depolymerisation kinetics shows an emergence of a bimodal pattern in the GPC chromatogram of subsequent intermediate MWD curves of most bio macromolecules such as multistranded polysaccharides such as Xylan and DNA duplex, Scleroglucan triplex etc. as reported by Stokke and Christensen and their co-researchers (1992-1996) and Hjerde et al. (1998a, b, 1999). Similar transformation of peak shape from unimodal to a bimodal trend was observed in the GPC chromatogram of cellulose-accelerated decay under various environmental conditions (Fig. 2.8 a-d), obtained from the thesis of Richard Heywood (1997). The second peak was found to increase as the degradation proceeds and was detected to contain more disordered (coil) conformation compared to the ordered duplex / triplex.
Fig. 2.7 a-d: Helical Folding (a) Cellulose backbone, (b) single, (c) double and (d) triple strand formation of multistranded polysaccharides (e.g. Xanthan, Pollulan, Schizophylan)
conformation of the main first peak. Interruption in the van der Walls interactions and hydrogen bonding among the neighbouring helices disrupt this vital cohesive forces that maintains the structural strength with conformational changes leading to helical to coil transition (Tanaka and Nkajima, 1972; Yanaki et al, 1985; Kitamura, 1989). Molecular modelling shows Xanthan displays similar backbone conformation similar to cellulose (Millane and Wang, 1990; Stokke et al., 1989; Deslandes et al., 1980; Rowland and Roberts, 1972; VanderHart and Atalla, 1984). The present computer simulation study will show this feature in the simulated MWD results in Chapter 3 and 6. The molecular mechanisms behind this will be elucidated.

Degradation study of Chitosan, a polysaccharide, has also exhibited a similar deviation from random scission to non-random scissions. A recent GPC examination (Boryniec et al., 1997) displays similar distinct bimodal features of the intermediate decayed MWDs (Fig. 2.9a-c) in variable conditions. It is postulated that the longer chains degrade with much a slower rate than the shorter ones, owing to the influence of supramolecular structure. The latter was shown to dominate the course of chemical (hydrolytic) (Fig. 2.9b) and bio-chemical (enzymatic) (Fig. 2.9c) decomposition by posing structural hindrance and co-operative resistance of the intra and intermolecular bonding forces similar to multistranded polymer complexes. The partial depolymerisation is caused by the regional differences in crystalline and amorphous molecular characters (Sashiwa et. al., 1993; Roberts, 1992) in Chitosan topology that result in the splitting of the initial peak as evident in the above polymers. However, this feature was not found in ionising radiation (Fig. 2.9a) induced chitosan degradation (Boryniec et. al, 1997), which seems to be random due to equal proportion accessibility throughout the polymer matrix.
Fig. 2.8a-d: Shows deformation of MWD curves presenting intermediate molecular states with progress of decay, (a) 120°C, (b) 140°C, (c) 160°C in Oil and (d) 160°C in Vacuum. All display lateral curve shifts, bimodality, curve broadening, peak-height loss, reducing shoulder/tail at high molecular weight end with reforming a sharp Gaussian distribution at the end of decay upon a significant shift to LMW end.
Degraded Chitosan in Variable Environment (GPC)

Fig. 2.9a-c: Shows intermediate changes in MWD curves as intact macromolecule degrades by (a) ionising radiation, (b) hydrolytic and (c) enzymic attack. All display lateral curve shifts, bimodality, curve broadening, high molecular end shoulder/tail reducing in the intermediate decay states characteristic to cellulose decay.
2.4.4. Degradation in a Complex Reactor

Large electrical transformers and cables in the power industry use fibrous paper insulation impregnated with mineral oil as electrical insulation. The paper material used is made from delignified wood pulp. The commercial cellulose based papers contain approximately 90% cellulose, 2-3% lignin and a balance of hemicelluloses. The latter are water-soluble polysaccharides similar to cellulose. Lignin is a polymer with phenylpropane units, linked to each other by carbon-carbon and ether bonds. It forms complex structures with cellulose through hydrogen and ether bonding (Watanabe et al., 1989). The inter-molecular and intra-molecular hydrogen bonding forces and the percent of crystallinity in the overall structure mainly contribute to the tensile strength of the paper. The combination of paper and oil provides better insulation with a higher dielectric constant than either one alone. As a cheap source of insulation and because of its inertness to the oil, cellulose is preferred in place of a synthetic material. A typical 500MW transformer contains 10-12 tonnes of paper, 30-120 mm thick (density 0.7-0.8kg/m³) in 45 tonnes of oil (Emsley and Stevens, 1994a, b).

The paper is known to deteriorate under the influence of heat, oxygen and moisture and physical stresses, generated by thermal, mechanical and electrical transients. The initial DP of the cellulose is in excess of 20,000 monomer units in the natural state, but is dramatically reduced in the course of processing to 1000 - 1300 (Fallou, 1970) and further reduced to 950 during drying of the transformer (Shroff and Stannett, 1985). Thereafter ageing in service reduces it further. The paper is expected to be operational throughout the lifetime of the transformer (25-40 years), but, at a DP below about 200 to 150 its mechanical strength has reduced to ~20% of its initial value and paper is brittle and vulnerable to damage (Fabre and Pichon, 1960). This point is regarded as the end of life criterion for transformer insulation. It has been generally accepted that a 5.5°C raise in temperature halves the useful life of the paper (Karsai et al., 1987) and ageing of the paper insulation determines the ultimate life of the transformer, although
other factors may cause it to fail early. In order to predict the life of paper insulation within a transformer, it is important to understand the chemical processes of cellulose degradation. This would also assist in the development of insulation monitoring methods. Other factors such as condition of the oil, its degradation products (acids), electric fields etc. are of secondary importance (Fallou, 1970).

A number of laboratory studies of paper insulation ageing under simulated transformer operating conditions have been reported (Emsley 1994a, b, Shroff and Stannett, 1985; Moser and Dahinden, 1988). Degradation kinetic rate constants relating to the DP of different cellulosic materials have been reported for different environments (oil, moisture, air, oxygen-free atmospheric). The earliest experiments by Fabre and Pichon (1960) indicated that the DP decreases linearly with ageing under any of the three main degrading agents - temperature, moisture and oxygen. The latter two were found to be by-product of degradation of both paper and oil (Shroff & Stannett, 1985; Moser & Dahinden, 1988). The degradation has generally been regarded as a totally random process. Early mathematical (statistical) kinetic models developed by Kuhn (1930), Freudenberg et al. (1930), Ekamstam (1936), Sharples (1957), Emsley & Stevens (1994a, b) Zou et al (1994) assume a random chain scission reaction with a constant bond scission rate. These simple models yield zero or first order kinetic characteristics and have been successfully applied to cellulose under certain conditions. More detailed studies of cellulose degradation have shown that the kinetics is better represented by the following non-linear function of time (Emsley et al, 2000b; Emsley and Heywood, 2000), This is consistent with a complex reaction scheme of competing reactions.

\[
\frac{1}{DP_t} - \frac{1}{DP_0} = \frac{k_{10}}{k_2} (1 - e^{-k_2 t})
\]

Where \( k_{10} \) and \( k_2 \) are constants and \( DP_0 \) is the initial DP.
2.4.5. A Multi-rate Model – New Perspective

(Fig. 2.10)

The ageing process of cellulose can be regarded as an ideal example of 'polychromatic' kinetics illustrated in Fig. 2.10 when subjected to attack by several reactive accelerators (moisture, oxygen, acids, morphology or structure and the other secondary effects) and conditions (air, oil, Vacuum and range of temperature). The most ordered structural macromolecules start to disintegrate into disordered arrays similar to multi-stranded polysaccharides. The transformation trajectory goes through the similar strategies to reach the end state via a few intermediate states. The Emsley-Heywood kinetic equation derived from the experimental results shows that the linearity of the reaction velocity is governed by the deviation of the parameter $k_1$ from its normal uniformity as reflected by $k_2$. This reflects the dynamics of the changing state of the system, where one state evolves from the previous one in a long series of molecular events, influenced by regional rate variability. The new generation of degraded chains yields intermediate oligomers and Furfurals.

Computer simulation in this project has been optimised with an ultimate aim of integrating various simple degradation models to create the above complex multi-rate kinetics of cellulose polysaccharide biopolymers. The stages of developing simulation methods are detailed in next few chapters.

The end products are a mixture of monomeric species (decomposed into various furan and furfural compounds) and a series oligomers daughter products of the cellulose parent chains derived via different pathways with different reaction kinetics through $k_1$, $k_2$, $k_3$ etc. No definite solution has yet been reached to pinpoint the actual mechanisms. Furfural is an important product for monitoring the ageing of transformers, since it can be isolated from the oil and analysed by HPLC. Once formed it is either degraded to other products or partitioned between the oil and the paper. An empirical correlation with DP (Burton et al., 1984, 1988; Shroff & Stennett, 1984) showed Log (DP) is inversely proportional to furfural concentration. A direct
Cellulose Decay in Electrical Transformer: Kinetic & Structural State Changes

Fig. 2.10

Multirate Model of Cellulose Degradation

- Scission rate $k_0$
- Scission rate $k_1$
- Scission rate $k_2$
- Scission rate $k_3$
- Scission rate $k_4$
- Scission rate $k_5$

End Products

- $k_{1t}$
- $k_{10}$

End State

- TIME 1
- TIME 2
- TIME 3
- TIME 4
- TIME 5
- TIME 6

Oligomeric products

- Unit Monomers -building blocks
- Furfurals

End time

- Amorphous
- Semicrystal
- Crystalline
correlation of the latter with the mechanical properties of the polymer (e.g. tensile strength) could be another alternative, but is difficult to achieve, due to scatter in the data (Unsworth and Mitchell, 1990).

The above diagram (Heywood, 1997) shows how tensile strength “TS” represents a physical parameter of cellulose material that can be influenced by average degree polymerisation “DP” - a structural attribute. The latter can provide information measuring the extent of deterioration caused to the former via nonlinear changes of the reaction rate constant ($k_1$).

### 2.4.6. Contribution of SEC

SEC has been used in many modern investigations to characterise the complex polymer temporal behaviour of ageing polymers (Emsley and Heywood, 2000; Tian et al., 1998; Shaw and Tuminello, 1994; Tobita, 1998). The SEC method separates polymer molecular fractions by size (strictly by hydro-dynamic volume) and provides MWD and various molecular averaging parameters as an output. It can be used to generate molecular weight distribution profiles of the polymer as they change with ageing time. The pattern of bond scission, whether totally random or preferential will affect the chain-length distribution of a polymer (polydisperse), generally increasing the polydispersity ratio. Thus the Molecular Weight Distribution (MWD) profile of any polymer population undergoing decomposition, obtained for instance from a lab SEC measurement, gives an account of the reaction behaviour and progress for the whole system. It provides important anatomic information regarding initiation and spreading of structural decay in
Chapter 2: Polymer Degradation

different reaction zones in more detail than can be available from just an average DP measurement alone. Thus it is hoped that reversed-engineered chromatogram simulations will provide an insight into degradation mechanisms and kinetics that would otherwise take months or years of lab experimentation to elucidate.

2.4.6.1. **Interpretation of MWD curve attributes**

Experimental evidence suggests that not only the pattern but the number of bond scission per unit time is a function of degradation time. Examples of such behaviour are found in the literature for polymers such as cellulose and other branched chain polysaccharides - xanthan, dextran; polyolylfins - polystyrene, polyethylene etc. Simulation models of basic random and cut-in-half type degradation have been reported (Guita and Chiantore, 1990; Plaumann et al., 1987a, b; Schichuk and Lutsyak, 1993; Viebke et al., 1994). The ratio of $M_w/M_n$, dispersity index, reflecting MWD changes during polymer ageing, is often used as a guide of homogeneity of the degradation process. It has been shown that, if this ratio remains fairly constant (Zou et al., 1994), it is indicative of the degradation mechanism being purely random and not preferential. Guita and Chiantore (1990) have further shown, in the case of random degradation, that this ratio approaches a value of two and remains constant independent of any recombination of fragments.

Alternatively, if the scission occurs near the centre of the molecule, the ratio decreases. Other kinds of preferential breakdown, such as in the higher molecular weight or lower ranges also produce distinctive MWD curve changes. For instance, Viebke et al (1994) concluded that chain chopping occurred initially in the high MW molecules. However, Cosgrove et al. (1985) proposed that low MW cellulose chains degraded faster, due to easier accessibility by hydrolysing reagents. However, visual inspection of his MWD curves seems to support the opposite - which the higher molecular weight degraded first and then progressed towards the lower end. These sorts of options will be examined in this thesis (see chapter 6).
Recent studies of accelerated ageing of cellulosic materials also reveals emerging multi-modal patterns of distribution during ageing, indicating a non-homogenous and preferential breakage of higher molecular weight / longest chain regions. These observations of (Heywood thesis, 1997; Emsley and Heywood, 2000) are also supported by the findings of Hill et al. (1992, 1995a, b, 1996), Cosgrove et al. (1985) etc. Peaks progress towards the lower molecular weight region through a series of ever broadening peaks. Striking similarity is found in the case of a polyester melt (Miller et al., 1991) and a standard polysaccharide (Emsley and Heywood, 1995). Hill and his co-workers (1992, 1995a,b, 1996) concluded that bonds near the middle of the chains have a higher probability of rupture than those near the ends. They suggested the existence of two different kinds of links in the polymer population normal or weak links. The latter are more susceptible to break or accessible to the reagent. In semi-crystalline materials like cellulose, it is thought likely that they occur at the chain folds in the disordered regions. Thus scission mechanisms could be a combination of both random and preferential. This simulation results in Chapter 6 will examine these effects in details in terms of progression pattern of MWD curve profile and show the extent of information that can be gained to the prediction of polymer durability and shelf life. Averaged attributes such as poly-dispersity indices (DPd/DPw and DPw/DPn) are plotted against time as rate curves and compared to predictions of others (Chiantore and Guita, 1993; Zou et al., 1994).
2.5. Conclusions

The structure and morphology of naturally occurring polymers of very high molecular weight, such as cellulose, starch, enzymes, silk, jute etc. are varied and complex in nature. As a result, adequate structural determinations only began to appear in about the middle of 19th century and the decomposition behaviour of these substances remains obscure. The advent of modern chromatographic methods and computer simulation models has facilitated the investigation of individual polymerisation or decomposition mechanisms. MWD plots contain detailed information on chain distribution changes during ageing, but are difficult to interpret. A detailed analysis that relates changes in the MWD to structural integrity changes in molecular structure, damage to physical state, decrease or increase in polydispersity would provide a powerful tool for understanding the degradation process. Each individual polymer has its own characteristic decomposition mechanisms and kinetic behaviour and the simulation algorithms in this study attempt to model some of the more common mechanisms.

A bond scission in the primary covalent backbone structure of a synthetic or natural macromolecules reaction not only depends on chemical factors e.g. activation energy barriers, structural/steric hindrances, but also on structure factors. Additional co-operative forces operate in a polymer, which maintain its morphological integrity, such as hydrogen bonding and molecular entanglements. Scission rates of chemical bonds are dependent on temperature and on absorption of any external energy in the form of light / photons / higher energy radiation and thermolysis and pyrolysis of polymers and plastics are of particular commercial importance in investigating polymer modification processes (Schnabel, 1981; Grassie and Scott, 1994). The higher order of packing of most bio-polymers such as polysaccharides, protein, genetic materials strengthens their thermal stability relative to man made plastics or fibres. Bond rupture in a polymer instigates a whole range of changes from conformational or thermodynamic transformation to
diffusional and structural deformation. However persistent cleaving of bonds under thermal influences eventually destabilises this resistance and destroys morphological integrity. This leads to crystallographic transitions in the melting and glass transition temperatures of the crystalline and amorphous polymers, and thermal denaturating of bio-macromolecules (Grassie, 1956, 1959; Madorsky, 1964; Schultze, 1974).

It is the aim of this work to produce computer models of the most common macro-scission processes and use them in combination to model the complex processes occurring in real systems. Most of the experimental work is based around the degradation of cellulose, because of its high commercial importance, particularly in the paper and electrical industry (where it is used as electrical insulation). A further reason for using cellulose as the example is the ready availability of MWD data from recent SEC measurements made during accelerated laboratory ageing tests (Emsley and Heywood, 2000).
Chapter 3

Monte Carlo Iterative Modelling Of Polymer Chain-Scission

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3.1. Introduction

Computer simulation modelling alone or in combination with the Monte Carlo method has been proved a very powerful tool to study complex macromolecular systems in detail and provide insights that would have been difficult to gain otherwise. The general progress on use of Monte Carlo (MC) computation began in the late forties, invented by Von Neumann and Ulam (Marshall, 1956). The efficiency of a Monte Carlo method depends on the efficiency of its algorithm. The algorithm can be designed retaining its inherent simplicity or can be adapted to more robust form through skilful incorporation of probability functions. This would then enable a rational translation of an unclear system into probabilistic terms and treat it directly as a sequence of probabilistic problems. A numerical solution approach is usually used to simplify a practical problem that avoids solving difficult analytical equations. This technique is popularly applied in polymer studies such as polymerisation (Krentsel et al., 1997; Yang et al., 1988a, 1988b, 1990, Tobita, 1993a, 1993b, 1993c, 1994a, 1994b, 1994c, 1996c, 1998), degradation (Plaumann, 1987; Rapoport and Efros, 1994, 1995; Radiotis & Brown, 1997; Huang et al., 1995; Tobita, 1995b, 1996a, 1996b) and various property assessment of polymers such as investigation of hydrophobic interactions (Dashevsky and Srakisov, 1974; Owicki and Scheraga, 1977; Matsucka et al., 1976; Swaminathan & Beveridge, 1979; Okazaki et al., 1979; Pangali et al., 1979), structure-reactivity aspects (Balaban, 1980). A number of analytical models (Saito, 1958; Suwanda et al., 1988b; Tzoganakis, 1988; Ryu, 1991; Triacca et al., 1993) of simulation of the MWD changes of synthetic polymers have tried to make a comparative study with GPC experimental measurements. Each model is limited to a particular case and not suitable for a global application. In comparison attempts in computer modelling of polymer degradation study are very few and are far more limited in capacity. Though Monte Carlo style algorithm impart more flexibility to computer simulation study in dealing with theoretical simulation of polymer properties, but the areas of polymer degradation still remained relatively inadequately explored. This is what is aimed to achieve in the
current project. The computer simulation will be extended to a global large-scale application. This chapter will describe the step-by-step development of a computer program and scission models with some examples of their end results. The latter will show the different patterns emerged in MWD curve sequences with progress of partial decay process depend on various scission parameters and initial distribution of intact polymer.

A number of non-uniform probability functions were investigated for better adaptation of Monte Carlo (MC) probabilistic algorithm. These will be described fully in the later sections together with an illustration of the use of computer interface strategy in making the simulation experiment user-friendly, flexible and easily adaptable to incorporate complex algorithms. The further development of the computer program and advanced modelling study will be discussed in next few chapters. The ultimate goal of this chapter is to exhibit how simulated MWD temporal curve features were optimised with a clear and readable appearance as an initial phase of development and the desirable lateral curve shifts (similar to GPC curves) were achieved by means of a suitable probability scheme. Finally, the concept of a more extended design of MC method will be discussed including the way of implementing the concept to propagate a dynamic network of simple scission models. This was called as Slider I model where Slider I computer interface was designed and utilised as vehicle of the model operation.

3.2. Scission in Polymer Matrix

A polymer system is assumed to consist of wide variety of chain sizes and hence is polydisperse. The reactive aggregates containing chain-lengths of different magnitude are the compositional vectors that may reside anywhere along a three-dimensional complex of an ordered assembly of a polymer surface. A scission may takes place at a site along the long backbone of a linear chain situated in any one such assembly. A scission event is triggered when an intact polymer surface is exposed to an aggressive agent or a
stable chain conformation is perturbed via thermal vibration or other means resulting in breaking up an intact parent chain into initially two smaller chains followed by further indefinite fragmentation. The degradation chemistry was discussed in Chapter 2. The subsequent fragmentation depends primarily on the extent of physical damage caused to the adjacent area. There are different ways to incite a chain to rupture. How different sized polymer chains divide into two or more fragments during the course of destructive reactions is important. The patterns and spread of this division may take distinct complex form as they belong to differently located aggregates with different kinetic potentials in the complex structure. Their MWD profile can trace the corresponding proportionate changes to implicate alterations in the polymer's physical and chemical properties. For convenience of keeping a record of many hundreds of thousands such scission events and simplicity, it is necessary to imagine only simple forms of breakdown processes as stated below.

### 3.2.1. Simple Scission Models

**Random time:** This model allows a fully random breakdown process. A chain can be randomly selected from the total chain size population and a rupture may occur at any site. So all the chains are equally liable to break and so are the bonds contained in each. Random chain scission is characteristic of oxidative degradation reactions (Jellinek, 1955). The probability of bond breaking is assumed uniform in this case for each chain category in the polymer matrix.

**Cutinhalf:** The chain selection is fully random as above but bond-site selection for scission is limited to only the middle of the selected chain. Thus this type of cleavage attempts to slice a chain in two equal halves. This kind of breakage is quite common in mechanically stress induced polymer chain breakage (Florea, 1993; Nguyen, 1994; Odell and Keller, 1986), and by ultrasonic radiation (Price and Smith, 1993; Van Der Hoff and Gall, 1977). Polydispersity of the degraded polymer always retained a limiting value.
lower than 2 which is found typical of the shear-induced degradation, where scissions are favoured near the central location along the length of the molecule (Chiantore and Guita, 1993).

**Cut and Chop:** A randomly selected chain can be broken at the middle as above, however this cut is followed by a further chop of one monomer unit or more. This breakdown may be encountered occasionally in certain groups of polymers (e.g. condensation polymers), yielding reactive end groups for further degeneration. This mechanism is assumed as a combined derivative of partial unzip and percent cut (described below) in the present project and one of the multiple items comprising the complex scission network of cellulose or cellulose-like polymers at low temperature decomposition.

**Cut fixed length / percentage:** A random chain selection followed by an end cropping at a site measured by a fixed distance or a constant percentage of the selected chain-length. The crop can occur at either end of the chain. Chain end scission is characteristic of thermal decomposition e.g. Poly (α methylstyrene) (Madras et al., 1996, 1995; McCoy and Madras, 1997).

**Unzip:** This is same as above except that the fragment chopped away from the end is reduced to its monomer unit constituents and hence is assumed to disappear from the system. Unzipping implies that the chopping process continues along the backbone for some random distance. This kind of depropagation of oligomer fragments is also characteristic of thermal degradation or specifically in pyrolysis (Lehrle et al., 1996) and predominant in a number of synthetic polymers e.g. polyethylene, polypropylene, polyisobutylene and also in some biopolymers e.g. BIOPOL, cellulose and other polysaccharides (Grimbley and Lehrle, 1995; Chiantore and Guita, 1993).

In radical initiated decomposition, a fast chain reaction usually occurs after the first scission. Usually an initiation of a highly reactive micro-radical...
species gives birth to highly reactive macro-radicals. This chain reaction continues until the radical reduces to too small size to volatilise or terminates by either radical combination or disproportionation. For example thermal degradation of poly(methyl methacrylate), where after the homolytic fission of one bond, the chain depropagates or unzips as follows:

![Diagram](image)

However, general unzip only allows a randomly chosen extent of depropagation each time a molecule reacts. Following a cleavage, a random number of monomer units can disappear from each fragment. This mechanism can be viewed simply as volatilisation of a chain segment.

Both the above mechanisms - 'Unzip' or 'CutFixedPercent', may explain the intra-chain radical attack on a polysaccharide (Golova (1957), Kislitsyn (1971), Gardiner (1966), Byrne (1966), Shafizadeh (1979). The zip off mechanism is highly prevalent in other polymer autocatalysis (Simon, 1992a, 1992b, 1990; Ranzi et al., 1997).

**Weak link**: Weak link degradation mode models a situation where certain links in the chain are more reactive than the others. The model allows random exposure of the weak links only for a scission reaction. Some workers believe that macromolecules are composed of two kinds of primary links – very weak or very strong. In semicrystalline polystyrene (Grassie & Scot, 1994) and cellulose (Chang, 1971), weaknesses are caused by folds in the polymer secondary structure. Presence of weak-links is evidenced in enzymatic (Stokke et al., 1992), thermal (Yanaki et al., 1985) attack and acid hydrolysis (Christensen et al., 1993) of multistranded polysaccharides. The occurrences of the former at some persistence length gradually make the very stable ordered conformation of these polymers vulnerable to
progressive attack and thus unstable which finally reduces into disordered coil fragments. During hydrolysis, the reagents first attack hidden labile weak-links. This leads to severe deterioration of the secondary structure. The aggregates lose their internal integrity. In thermally driven environment the loss in weaker inter-chain linkages are more extensive with the loss in the cohesive forces. This has more potential in lowering the overall activation energy for bond rupture (Cameron and Kerr, 1970). Evidence of Weaklinks was actually detected by FTIR in thermal degradation behaviour study of polypropylene (Chan and Balke, 1997).

3.2.2. Analogy with a Pearl Chain (Fig. 3.1- Fig. 3.3)

An analogy of polymer chains with pearl chains helps to give a simple illustration of chain-splitting mechanisms and their numerical and combinatorial implications. The diagrams in next few pages describe these processes more clearly. Each pearl bead represents a unit monomer, called the building blocks of a polymer chain. Polymer chains like pearl chains are composed of multiple units like pearls and links (called bonds in chemical term), which hold them together (Fig. 3.1a-b). Initial chain length or molecular weight distribution (PCLD or MWD) of polymer (Fig. 3.1c) may take a definable form of either a non-uniform distribution form such as Normal/Gaussian, Skew or Gamma / Beta etc. or an uniform such as random Boltzman / Flory distribution. This is unique to a polymer system and mostly depends on their structural hierarchy e.g. linear or branched or multistranded (discussed in Chapter2, see Fig.2.1a-b, Fig. 2.7a-d). Upon undergoing partial and gradual degradation, the polymer start to loose its levels of ordered architecture, which can be exhibited in their degraded MWDs through the emerging pattern of deformity of the initial distribution. Successive temporal behaviour of the latter with newly generated chains is depicted in Fig. 3.1d. In degradation reaction chains are usually cleaved at a link or bond site to yield two shorter new chains (Fig. 3.2a) or in some cases two cleaved fragments may come in contact to recombine yielding a longer new chain (Fig. 3.2b). Scission mechanisms can be summarised in two main
Analogy with Pearl Chain and Polymer Chain length Distribution (PCLD) - basic concept

What are Polymer Molecules? - basic idea

Polymer Backbone

Bond

Unit

Monomer

Monodisperse: distribution consists of equal size polymer chains

Polydisperse: distribution consists of unequal size chains

What are Polymer Molecules? - like a chain of pearls

Imagine a collection of many different length of pearl chains (say 10000 or more) - represents a polymer system

Figure 3.1a-d: illustrates (a) a simple linear polymer chain, (b) analogy with pearl chain, (c) how chain size distribution in polymer system was plotted in two dimension in the current model, (d) how temporal reaction progresses are reflected in generating a set of overlapped MWD curves in succession as the initial curve shifts from high molecular weight region (on LHS of the plot) towards low molecular weight region (on RHS of the plot).
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**Polymer Chain Scission**

- Polymer chain scission process - imagine a pearl chain is cut at any link or links - will give two or more shorter chain lengths as shown below:

  **Original Pearl Chain Length**

  - Link is cut
  - Link is cut again

  **Polymer Chain Scission Mechanisms** (Central Cleavage Process)

  - "Cut in Half" chain scission process: chains split in half only. Two cases:
    1. for odd chain length two fragments thus generated are not equal
    2. for even chain length, they are equal

  **Original Polymer Chain Length**

  - Link is cut in two even halves
  - Link is cut in two odd halves

**Polymer Chain Recombination**

- Polymer chain recombination process: Similarly any two chains can form a link in between and make a longer length chain:

  - a new Link is formed
  - a new Link is formed

  **Polymer Chain Scission Mechanisms** (End Chopping Process)

  - "Unzip" chain scission process: a portion from the either ends of the chain can be chopped away. The smaller portion is assumed to completely broken down into its constituent beads (unit monomers) and vanished from system

  **Original Polymer Chain Length**

  - portion unzipped from this end and vanished
  - portion left only if the length is above critical length (300)

  - portion unzipped from this end and vanished as too small
  - portion unzipped from this end and vanished as too small

---

Fig. 3.2a-d
categories – a chain is either cut in the middle along its length such as in ‘CutInHalf’ (Fig. 3.2c) or chopped at an end (Fig. 3.2d) as in ‘CutFixedPercent’. The ‘Cutchop’ and ‘Unzip’ scission can be interpreted in terms of partial or total volatilisation of smaller fragments. Thus a chopped section may evaporate partially or wholly from the system. Hence either or both of the newly generated fragments are counted in the MW distribution and fragmentation continued until a critical length is reached in some polymers (e.g. cellulose, Xylan etc.). The kinetic behaviour of such cases dictates that fragmentation stopped upon reaching a limiting stage. Different length chain may reach this stage at different time. The limiting stage or a DP$_{\text{min}}$ is exhibited by a number of macromolecules such as polysaccharides (Stokke et al., 1992; Yanaki et al., 1983; Christensen et al., 1993, 1996; Hjerde et al., 1998a, b, 1999) and DNA (Thomas, 1956). The DP$_{\text{min}}$ was detected in cellulose thermal decomposition study as 200 (Emsley and Heywood, 1995, 2000, 2000b). In the scission models this limiting DP is simulated by imposing a lower limit to the most probable new generation of fragment sizes at the end of each time cycle. Fragments under this limit are not allowed to undergo further decay. The smaller fragments may undergo a complete/partial unzipping (depending on temperature) withannihilation of product monomers. This eliminates undesirable scatters at the low MW end.

In contrast, the ‘Weaklink’ mechanism is a recurrent one and can occur in both the middle and the end of a chain. Hence occurrence of weak-links (Ranby, 1961) along the chain backbone is uncertain and so is their frequency. Possible location of weaker links (Chang, 1974) are thought to be in the chain folds, disordered end arrays of ordered chain helices or stressed irregular arrangement of the amorphous regions of polymer complex assemblies (Fig. 3.3a). Figures 3.3b-d presents flowcharts of step-by-step development of the degradation algorithm for a fixed period of time. Iterative algorithm originated with Emsley’s (1995) initial simple scission models (Fig. 3.3b) was further developed into a Monte Carlo dynamic model – Slider (Fig. 3.3c) and a semi-iterative mathematical model (Fig. 3.3d) that enhanced the slow arithmetical progression counting process by converting into a direct instant calculation using an algebraic-statistical expression. The
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Fig. 3.3a-b: (a) 'Weaklink' Locations, (b) Flowchart of Emsley's Iterative Model Algorithm

Polymer Chain Scission Mechanisms
(Weaker links - at chain-folds, loose ends, stressed positions)

"Weaklinks" chain scission mechanism: This depends on 3-dimensional structure and aggregation of chains as they closely knitted together to form very highly ordered assembly. Highly ordered regions are denoted as crystalline - crystallite fibrils. Less ordered regions are designated as semi-crystallites with loose ends and lots of stressed links (weaker ones) to break easily. Disordered regions are referred as amorphous or non-crystalline.

Iterative Random Model Algorithm (general flow chart)
Initial distribution (Gaussian, skew or experimental) defined as Array - its index present chain lengths, contents presents corresponding numbers

Define another two dimensional arrays to store total number of molecules and bonds and their corresponding outer time-cycles (PDCycles), starting with zero time

Repeat for a number of preselected outercycles

Selection of a bond from the selected chain to break, by either picking a random number from the total number of bonds in that length or a pre-selected one

Run the appropriate degradation (simple chain scission model) function to complete the reaction operation (systematic / random). Update the distribution array by adding the newly generated fragment/s number to corresponding length index / indices' contents and subtracting one from the original selected one. Update the total molecule / total bond arrays accordingly.

Repeat for a number of inner cycles (10,000,000)

No

YES

No

Plot Distribution per each outer cycle completion

YES

Plot Final Distribution
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Fig. 3.3c-d: Flowchart of (c) MC Slider, (d) Exact Algebraic Statistical Model Algorithm

Iterative Slider II Model Algorithm (general flow chart)
- Define 2-dimensional arrays for storing initial chain length distribution and outer time cycles.
- Arrays for storing and updating total number of molecules and bonds per each time PD cycles.
- Selection of chain length population subsets to attach rates via slider II.
- Repeat for a number of preselected time segments.
- Bond positions are preslected as user defined from slider II interface, which will only be degraded per each iteration cycles.
- Calculate the probability rates of chain scission for all subsets per each time segments, calculate total number of bonds to be degraded per each subsets per each time segments as guided by slider II selection.
- Degrad three bonds using appropriate selection processes as guided by bond locations given in slider II interface.
- Plot Distribution per each time segments.
- Plot Final Distribution graphs.
- Compare with experimental data.

Semi-iterative Mathematical Model Algorithm (general flow chart)
- Define 2-dimensional arrays for storing initial chain length distribution and outer time cycles.
- Arrays for storing and updating total number of molecules and bonds per each time PD cycles.
- Define a probability distribution function (continuous) for the entire chain population.
- Apply an algebraic function generated in terms of above exact probability to calculate the resultant length distribution element-contents, (which has taken account of bond location and bond scission mechanisms). This calculation is instant for a number of inner cycles.
- Repeat for a number of preselected time segments.
- NO
- YES
- Plot Distribution per each time segments.
- Plot Final Distribution graphs.
- Compare with experimental data.
latter uses geometric progression and algebraic induction methods. Slider model will be described later in this chapter and the maths model in Chapter 5. Fig. 3.3b illustrates the huge number of iterations involved in the original model for calculating subsequent generation of MWD by means of a simple arithmetic progression, which were reduced enormously in the developed models (Fig. 3.3c-d) with added robust form, structured with levels of weighted and transition probability functions. This is further described in more details in later sections (see Fig. 3.17).

3.3. Improvement of Initial Algorithm

The basic model developed by Emsley and Heywood (1995) used an iterative algorithm, consisting of many thousands of iterations, each employed to break a chain in two fragments in a random or systematic manner. This means ideally that one chain of any length from the total molecular population must be selected for breaking one of its bonds at any location along its total length. The method used a uniform random number generation from the total chain sizes to mimic random selection of a chain. It assumed chains are equally probable to attack at any time irrespective of any structural or configurational differences. Chain sizes and their frequency ratios were stored in a two-dimensional array, per each main outer time cycles (Fig. 3.3b). Each of the latter consisted of a fixed equal number of inner cycle-units each of equal duration, which were incremented by one unit after each scission. The number of time cycles can be set before a simulation model run. An initial polymer distribution of Normal or Skew type was used as representative of a theoretical intact polymer system. The two new fragments, generated as a result of a chain cleavage, were then recorded in the respective size array, so that the new generation of fragments can themselves be degraded as degradation proceeds. This operation is repeated over many unit time cycles. The latter ranges from an interval of 1 to 100,000 of inner cycles that is calculated by multiplying cycle length with an arbitrary integral constant (10,000). The cycle length constitutes the interval between two time-cycles and remains constant for all
time-cycle intervals. The algorithm was maintained in linear scale for calculations MWD distribution and the other related attributes.

The advantage of this model is that it is very simple and easy to implement and provides a suitable basis for further development. The disadvantage is that the model does not allow for the complex nature of macromolecules and their decay processes that take place in reality, which may contradict the assumption of equal probability given to all categories of chain-exposure processes (McDermott et al., 1990; Train and Klein, 1988; Huang et al., 1995; Schiichuk and Lutsyak, 1993). A non-linear breaking probability is adopted in the latter references, where uniform probability of breaking was found inadequate. The same was found preventing from displaying the expected lateral shifts in the subsequent evolution of MWD curves.

The model assumes at each inner-cycle one chain must be broken and in only two fractions. In reality each unit time may bring about none or one or more than one chain rupture (see Poisson time distribution model concept in Chapter 7). Similarly more than one bond may be broken simultaneously at any single instant of chain scission. The initial model does not include any parameter to vary the inter time-slice distribution of the total allowed decay time. This enforces a uniform or constant number of bond scissions per each unit time constituents with a constant duration. The modified model was enhanced with implementation of this parameter that could impose variability and more control on a number of bond scission related attributes transforming to more authentic ones. In practice the molecular disintegration is a time dependent process and as such time spent to complete one or more scission reactions may vary differently for each macroscopic time scale unit sequence (e.g. hour in case of cellulose decay). This dependence also involves the nature of the reaction site, energy barrier and type of reaction and behaviour of degrading entities. Likewise the probability of number of reaction-occurrences is determined by several factors such as the reagent-access that depends on the nature of the initiation centres; how rigid is the order of chain arrangements; the temperature and reactivity of the neighbouring chains or the generated fragments; how the chains are
arranged spatially. The latter factors were easily implemented in the modified model in terms of probability parameters executing a non-linear density function that enabled creating a closer emulation to reality. This is elaborated in the subsequent sections.

### 3.3.1. Incorporating a Monte Carlo Method

Monte Carlo (MC) method is based on the use of random numbers and probability manipulation. Generation of true random numbers was very difficult in the past, but modern computer aided random number generators make it easier. The latter perform a number of mathematical operations on the seed so as to generate unrelated numbers. In this project, a random number generated by computer was used to simulate any process where an event occurred on the basis of some probability. Use of different seeds such as the computer system clock, ensured that the processor's performance rating was maintained to generate uniform random numbers and to ensure their sequence was not repeated. Monte Carlo algorithm can be classified as static or dynamic. A random sequence of statistically independent samples is usually structured in a static method from a given probability distribution of possible states. Dynamic method on the other hand is more structured to generate a random sequence of correlated samples from a defined stochastic process.

Static Monte Carlo is the simplest method that allows random sampling of different scission mechanisms generating a random sequence of the scission events (see Slider I model in the later sections). The events are either rated with equal probability or governed by a defined probability ordering in this method. A chain selection is conducted at random from a defined domain of the total updated chain population obtained from the previous time-cycle. For each time cycle one such domain is selected on the basis of certain weighted probability scheme. The bond location selection is governed by the event itself. For example 'CutInHalf scission event would allow a bond location to be selected in the middle of the selected chain.
Similarly in the case of 'CutFixedPercent' the location would be at a preferred site near the end of a polymer chain. A variety of derivatives of the scission mechanisms are simulated by means of generating uniform or non-uniform random numbers (described in later sections). In this manner a network of the generated scission models is devised and their integrated application is tested in the resultant MWD curve patterns. This method thus allows simple probabilistic application of random numbers while still allowing an overall random sampling procedure of the system.

The dynamic Monte Carlo method was employed to import further expansion to the above where concepts of creating degradation zones of varying degree of reactivity and locations along the polymer complex. Per each turn of new time-cycle a nucleation centre from the existing reactive components is either allowed to carry forward or stopped to apportion the same elsewhere around the matrix. The scheme differed in moderating a true stochastic process where each event occurs obeying some order of probability. Scission mechanisms were inherent in the definition of events that also regulated the selection of a chain. The time evolution of this stochastic process was simulated simultaneously starting from an arbitrary initial time taken as 'Zero' time when the polymer is in intact state, prior to start of any degradation. A transformation to real time is computed mainly using an experimentally determined pseudo-first order kinetic equation of accelerated cellulose degradation. A few other statistical formulations are also tested, such as a Poisson distribution, geometric and Rectangular Hyperbolic functions to correlate both time and molecular distributions to this effect. These are detailed together with application of the dynamic method in latter Chapters (5, 6 and 7).

Numerical simulation of a polymer system posed a particular challenge due to the enormous spread of length scales and time scales involved. Length scales varied from the dimension of a macromolecule of chain size consisted of 10 unit monomers to $10^{10}$ or more. Using logarithmic scale could accommodate this length range. For ease of implementing statistical computation and their resultant graphics a valid compromise was reached
by choosing a system size within linear dimensions of a much-reduced range than the characteristic size range of the actual system. Simultaneously, simulation of time scale units was made possible to vary over a wide range from microscopic order of e.g. \(10^{-2}\) s (Rapoport and Efros, 1995) to macroscopic order of 1 - 500 hours (Emsley and Heywood, 2000) depending on polymer type, reactor capacity, kinetics etc. Simulation of real time unit to characterise bond scission events for a particular system was found thus either entirely system dependent, indefinite quantity or can be invented in terms of a suitable statistical distribution. So the present task is to make a compromise by combining the latter with experimental observations of time kinetics. The next section examines such application in other cases.

### 3.3.1.1. Monte Carlo Modelling of Polymers

*Polymer high-temperature degradation and fracture model:* simulates formation of a number of micro-defects in various regions of an intact polymer when exposed to hidden catalyst impurities (Rapoport and Efros, 1995) to spread in multiple cracks that portrayed the oxidation phenomenon of polypropylene. These sites were randomly distributed as initiation centres for attack by the “jogger” radicals (micro-radicals). These small radicals diffuse through the lattice sites in random fashion through an arbitrary number of diffusion steps, where they collide with immobilised polymer molecules at random sites and transform into alkyl macro-radicals. The latter are then framed as more probable centres to create major cracks. Spatial propagation of the degradation was assumed here to progress by way of transitional diffusion of low molecular weight radicals, due to the restricted motion of the solid phase macro-radicals (Popov et al., 1991). The same can be transmitted in other solid phase system (e.g. cellulose, polyethylene, polystyrene) via thermal vibration in the absence of propagation of oxidative radicals. These spots were though chosen at random, but clustered to emulate a major crack regulated by a probability density function.
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Eventually, a catastrophic failure of the system is decided by the simulator on the basis of the time required to merge several micro-cracks.

**Concept of preferential model imported in the present work:** The above conception of creation of preferential 2-D sites for crack initiation events is utilised in the current model design, where sequences of micro-degradation zones are created and their propagation is tested in both random and preferential frameworks. The amplitude of propagation varies from one zone to another, influenced by their structural and physical characteristic and controlled by a time progression. The above example envisaged complex polymer decay process in terms of a series of simple molecular scission events. The succession of these events was simulated by a static Monte Carlo model. This is manifested via generation of a random sequence of statistically independent samples from a given probability distribution of possible states. The former can be accomplished via a random number generator that produces a random quantity from a uniformly distributed range in each event cycle. Random numbers generated by a computer can be associated with a probability rating function such that the number can decide which event from the sequence to be simulated next where an event occurs on the basis of some probability. The probability of the successes or failures of an event occurrence in the same time-cycle, taken from a selection of equally or weighted ranked outcomes can be determined if a certain inequality such as \( \xi < p \) is satisfied. A flow chart of the developed algorithm is illustrated in Fig. 3.1. A precise simulation of the real experiment with all information is not even necessary. This is obvious from the next two examples of MC simulation in polymer degradation.

**PVC microstructure changes on thermal degradation:** A number of NMR analyses have been carried out to determine the preferred sites for elimination of stable chlorine atoms of Poly-vinylchloride (PVC) coupled to changes in the distribution of polymer chain tacticity (Millan et al., 1991; Lara et al., 1989; Radiotis & Brown, 1993). Radiotis & Brown (1997) used a theoretical MC computer simulation of PVC microstructure changes from the
thermal degradation to overcome the limitation of NMR analysis. Their objectives were to verify the validity of these experimental studies concerning the magnitude of the changes in tacticity along the length of the polymer. Each particular sequence of stereo-configuration is detected to have a preferential initiation site. The extent of degradation was assumed to depend on dehydrochlorination of some atactic and syndiotactic sequences. The program incorporated only specific details of the system e.g. stereo-sequences, DP, number and frequency of different stereosequences, degradation sites, which were created using a random number generator. Conformations and length parameter details were stored in two separate arrays. Once the desired chain is constructed the degradation cycles continued at specified sites on a random basis. Hence each such cycle demanded an intensive searching time to find the desired sequence to degrade needing long CPU time.

Peroxide initiated degradation of Polypropylene: This stochastic MC model presents a good example of a systematic probabilistic study of a degradation process. Complex kinetic event oriented, thermal degradation (at 200°C) processing of polypropylene in its melt state was defined in terms of a Markovian random walk in N-dimensional space of polymer population of N species. This model portrays the temporal changes in MWD as resultant co-related N states. The partial degradation of this polydisperse, high MW polymer was modelled numerically. Transitions of the system from one state to another in unit time steps were determined via a series of transition probabilities, calculated from the kinetic parameters (McDermott et al., 1990):

$$P_{AB} = 1 - \exp(-k_{AB}\Delta t)$$

Where $P_{AB} =$ Transitional Probability, $k_{AB} =$ Reaction rate constant, $\Delta t =$ time interval for Markovian chain state transition.
Thus transition probability of the system for $\Delta t$ duration,

$$\text{Prob}_{\text{system}} = 1 - \exp\left(-k_i(NTNB)\Delta t\right)$$

$NTNB = \Sigma(n-1)\ [P_n]$ (the total number of parallel reaction / active bonds available in the system). Radical rate constants were included in evaluation of kinetic parameters:

$$[R^9] = \left[\frac{2fk_d[I]_0}{[k_i(NTNB) - k_d]}\right] \times \left(e^{-k_d} - e^{-k_i(NTNB)}\right)$$

Above two equations were connected to calculate transition probabilities:

$$\text{Prob}_{\text{system}} = 1 - \exp\left(-k_i\left[\frac{2fk_d[I]_0}{[k_i(NTNB) - k_d]}\right] \times \left(e^{-k_d} - e^{-k_i(NTNB)}\right)\right) \times (NTNB)\Delta t$$

A unit time $\Delta t$, initially devised to measure frequency of scissions per second, was made constant and selected to be $2.5 \times 10^{-5}$ seconds. However, the entire simulation took enormous CPU time as long as 70000 seconds (17h) on an IBM Risc6000 system running AIX Fortran.

The above examples demonstrate the flexibility of Monte Carlo methods that can be tailor-made to suit the system. Thus a large system can be sampled in a number of random configurations and data can be used to describe the system as a whole. An advanced statistical model based on the concept of Markovian random walk of MWD state changes will be described in Chapter 5 with the results of its application to model cellulose complex decay in Chapter 6.
Chapter 3: Monte Carlo Modelling

3.3.1.2. Dynamic Monte Carlo Modelling

A real system is usually modelled using a state history, in chronological order of the actual real system (Evans et al., 1967). The latter refers to description of all possible states the real system can hold in succession depending on certain fundamental physico-chemical characteristics of the actual system. The results of the simulation are validated by means of rigorous statistical treatment comparing a partial state history. The method is more explored in the areas of macromolecular structure - property relationships but not so in areas of polymer degradation. Two new mathematical approaches will be discussed in Chapter 5 those implementing this modelling principle.

3.3.2. Importing Graphical Clarity (Fig. 3.4- Fig. 3.6)

Few serious problems were faced in further development of the existing scission model algorithms. As mentioned earlier, the latter failed to produce the desired curve characteristics in the simulated distribution result plots. The existing model tends to generate inwardly reduced degraded curves with loss in peak height, but keeping the peak stationary at the central position as evident in Fig. 3.4a-d. It did not produce the lateral peak shifts and curve movement towards lower MW region as observed in practical MWD chromatograms obtained from GPC. The latter shows adequate deviation and lateral shifts in the degradation generated curves from the initial MWD curve progressing from High MW end to low MW end (see Figures 2.8-2.9 in Chapter 2). Hence in simulation results, the initial form of the intact polymer distribution, plotted in two dimensions, is expected to depart from the original Gaussian or other initial distribution curve attributes such as amplitude, elevation, and peak shapes. This departure in curve shift and pattern is essential in order to demonstrate the episodes of chemical changes due to advances in degradation reactions and the effectual physical deterioration in polymer substrate. The simulation model algorithm should aim to generate a set of such overlapping curves that would verify temporal changes in number
and sizes of polymer molecules. Different trends in curve shift pattern, displayed by SEC chromatographic plots, also depend on the polymer type and reactor environment. The shift trend reflects important clues as to the chemical events happening in the real experimental system.

The simple models used algorithms for bond scission events, which involved many thousands of iterative loops and fully randomised chain selection processes. Immense fluctuations and interference in graphic output might have been created as a result of random recurrent iteration as obvious in early simulation plots Figures 3.4–3.6. Firstly, the random searching process slows down the program running speed. Secondly, its random nature causes rough irregular curves with multiple interrupting peaks or baseline noises mostly at the low MW end. Thirdly, the fully random selection procedures used in the existing algorithm may be responsible for preventing the outcome of important lateral shifts. This in effect enforced the selection process biased to the highest frequencies. Hence a number of non-uniform probability constraints were tested on the improved models with a view to capture these curve changes in the end results. This will be discussed in the later sections. A number of initial developments were necessary to achieve adequate results from the simulation of the simple reactors. These are summarised in the next sections. The final development will cover a novel algorithm that combined use of probability schemes and computer interface strategies. A gradual development of introducing different probability schemes will be described in the following sections and more advanced mathematical concepts in Chapter 5 and 7.

✦ First stage development: Addition of a colour palette and implement the necessary codes to make a large selection of colours available (section 3.4.1.).
✦ Second stage development: Modify the chain selection algorithm by introducing non-uniform probability to enforce lateral shift (section 3.4.2.).
✦ Third stage development: Introduce a smoothing algorithm to obtain a finer curve plot and optimised output (section 3.4.3.).
Initial Development Phase 1: View of Program Output Prior to and After Colour Palette Implementation

Figures 3.4a-c: show examples of chain length distribution output (a) –(b) from the initial version (I.e. before any development) of the computer program, (c) after introducing elementary colour pixels, (d) after introducing a large colour palette containing 256 different colour hues to the program.
Initial Development Phase 2: Achieving Lateral Shift in the Intermediate Temporal MWD Curves via Implementation of Probability Structures – example 1

Figures 3.5a-c: Show progress in achieving the desired lateral shifts in PCLD decay curves from high (RHS) to low MW (LHS) field, (a-b) examples of early results with moderate shift, (c) example of final result with significant lateral shift using 'CutFixedPercent' scission mechanism. Note: as this was done before implementation of smoothing routine, the MWD curves appeared with rough edges.

Figures 3.6a-b: show decay curves after introducing non-uniform probability scheme for chain and bond selection (a) ‘Weaklink’ (b) ‘Unzip’ scission (before introducing curve-smoothing routine).
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- Fourth stage development: (a) Optimisation of simple random models to preferential models (section 3.4.4.). (b) Use of computer strategy (Slider I model) for testing the effect of combined model on MWD profile (section 3.4.5.).
- The results of the final enhanced models are given in section 3.5.

The inefficiencies in the initial state of the program were thus overcome through implementing the above features. Addition of colour-palette, structured non-uniform probability and an efficient smoothing routine to the computer program and scission algorithm enabled to achieve clear, readable and fast graphic outputs of simulated PCLD curves with a lateral curve shift effect as observed in normal GPC chromatogram. The effect generated by a colour palette is shown in Fig 3.5a-d as the first phase of initial development. Fig. 3.4a-b shows the black and white appearance of MWD plot and Fig. 3.4c-d shows the appearance of enhanced coloured output. The achievement of lateral curve shifts in the intermediate decayed MWD was achieved as a second phase of initial development (Fig. 3.5 a-c and Fig. 3.6 a-b). In the third phase of development an efficient smoothing routine 'Cubic Cspline' was implemented in the program. The smoothing effects of the latter are compared with the un-smoothed and line-smoothed counterparts in figures 3.7-3.15. The interface of a smoothing index parameter that controls the extent of smoothing is presented in Fig 3.16. The effects of both (a) and (b) from the fourth phase development are illustrated in the figures 3.18-3.24. A flow chart of the improved algorithm is given in Fig. 3.17.

3.4. Development Phases

3.4.1. Colour Improvement

A colour palette is introduced in the new model implementation to enable the use of separate colour codes for each resultant MWD curve and for their further experimental graphics and charts. This adds enhanced readability
and clarity to the simulated curves and also makes their examination and analysis a lot easier. A curve smoothing algorithm has been devised to minimise the other visual interferences and noises. Examples of a few crude MWD graphs at the beginning of the development are shown in Fig. 3.4-Fig. 3.6 and the smoothed and enhanced graphs after initial development are illustrated in Fig. 3.18-Fig. 3.24 in the last section.

Only a few primary colours i.e. blue, green and yellow or black and white were available in the initial model. In order to expand the range of available logical colour hues, a colour palette was implemented in the program. The palette provided 255 colour hues. The CPalette class encapsulates a Windows colour palette. A palette provides an interface between an application and a colour output device (such as a display device). Windows uses the application's logical palette and the system palette, which defines the available colours to determine the colours used.

When a hue is chosen from 255 hues, it is specified in the form of bytes, defining the comparative degree of strength of the three primary colours. The specified bytes of each primary colour are packaged into a data-structure form called 'struct' - constructing the RGB macro selects a red, green, blue (RGB) colour based on the arguments supplied and the colour capabilities of the output device.

```
COLORREF RGB(
    BYTE bRed,       // red component of colour
    BYTE bGreen,     // green component of colour
    BYTE bBlue       // blue component of colour
);
```

The intensity for each argument is in the range 0 through 255. If all three intensities are zero, the result is black. If all three intensities are 255, the result is white. Otherwise combining different intensities of colour components a gives wide variety of colour coding. The various chosen colour hues are defined in an array, addressed as 'dwcolour[x,y,z]'. The
latter stores all the definable properties for a particular hue from the colour palette to isolate and create the hue to be ready for operation. The scope for use of colour options has also made possible an increase in the number of outer time cycles.

3.4.2. Probability Schemes

3.4.2.1. Initial Scheme for Chain Selection

The first approach: - first divide the total chain size population into several strips. Then a random choice of one such strip, bounded by upper and lower limits, or even more than one is made per each outer cycle time-segment for a uniform random chain/bond selection. Let $Y_i$ be the sum of frequencies of the range from chain size 1 to ith size from the total maximum size say $I$ $(I=1,2,...i,.....I)$. $I$ is an ascending positive integer variable, representing a chain length size parameter. $Y_1$ refers to the total sum of the individual number or frequency of each ith chain index. A chain size was next selected by generating a random number from the total $Y_1$. In this case, this total is constituted from a portion of $Y$, such that $a \leq I \leq b$, where $I$ is restricted by an interval with a lower and upper boundary of $a$ and $b$ respectively. This boundary could also be chosen at random, but in this case the strips are preferentially selected from the higher MW regions to favour the gradual progression of the lateral shifts. Thus the probability $p$ that a chain size is chosen beyond this boundary is nil. So the general numerical algorithm follows as:

1. Select values for $a$ and $b$.
2. Sum the total frequencies pertaining to a molecular strip within the above bounds.
3. Generate $U$ – a uniformly distributed random number from the total such that $Y_a \leq U \leq Y_b$.
4. Set a counter $I$ to $a$; while $U \geq F(I)$ increment $I$ by 1.
5. Output $I$ as the chosen size to degrade.
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The second approach:- Similar to first approach but using a non-uniform random number generator in step 3. It was found that using a normal distribution did not create the desired enhancement, so needed the following modification.

1. Select a size strip between interval a and b.
2. Construct a probability density function of random number I in the above interval that is normally distributed.
3. Generate cumulative densities of the above and keep them in an array F(X) of (b-a)=l elements so that
   \[ F(i) = \beta_1 + \beta_2 + \beta_3 + \ldots + \beta_i \quad (i = 1, 2, 3, \ldots, l) \]
4. Generate U, test if \( F(i-1) \leq U \leq F(i) \)
5. Output I

Thus the above allows different sizes, falling within the chosen portion of the total size index and assumes different probabilities. For example the first lowest size (indexed 1) is selected with probability \( \beta_1 \), next lowest size (indexed 2) is selected with probability \( \beta_2 \), \ldots , lth size with probability \( \beta_l \) and \( \beta_1 + \beta_2 + \ldots + \beta_l = 1 \). If the size strips are chosen in the highest MW region during the initial period, the highest probability mass will be centred on the mean of the strip lengths. By allowing the cross section of interval to vary, i.e. with a suitable differentiation of the standard deviation of the normal distribution during successive time cycles, a wide variety of experimental options can be opened up to manipulate to the desired curve progression profile. However, step 4 implies finding the value of the integer i via an ‘invert distribution function’ procedure. The steps 1-5 are repeated many times as desired throughout the whole or part duration of an inner cycle aggregates as well as outer cycles. This seemed to work moderately well.
3.4.2.2. Initial Scheme for Bond Selection

However, in order to perform a scission a bond selection scheme is also important following a chain selection. In the above simple degradation models bond selection is predetermined except 'Randomtime'. For example - Cutlnhalf cuts a chain at the middle bond, Cutfixedlength cuts at a user-selected particular fixed distance from the end, CutfixedPercent chops the chain at certain fixed location predetermined by user given percentage of the chosen chain length etc. This generates multiple peaks by means of accumulation of fragments of the same size and other undesirable effects in the resultant distribution curves. One way to eliminate this problem was to discard the smaller fragments by including a size limiting routine. Alternatively, it is possible to keep the chain fragmentation processes under control as well as create reasonable variation among the bond selection.

The idea is to introduce a non-uniform random nature on the bond selection and fragment recording process in the degradation models. The following algorithm has been tried, which may follow from the above after step 5:

6. Generate a geometrically distributed random variable, \( X \), taking the value \( i \) with the probability \( \gamma_i \approx \alpha^{i-1}(1-\alpha) \) \( i=1,2,\ldots; \ 0<\alpha<1 \), \( i \equiv \text{chainlength} \).

7. Construct an array \( F(X) \) of \( K \) elements containing the partial sums of probabilities \( F(i) = \gamma_1 + \gamma_2 + \gamma_3 + \ldots + \gamma_i \) \( i=1,2,3,\ldots,K \) such that \( k<X \).

8. Generate a random variable \( U_2 \) from the sum total CDF (i.e. \( F(i) \)), test if \( F(i-1) \leq U_2 \leq F(i) \).

9. Output \( i \) as the chosen bond location to degrade.

The array \( F \) contains the cumulative distribution function of the discrete random variable \( i \) which takes values \( 1,2,\ldots,K \) with probabilities \( \gamma_1, \gamma_2, \gamma_3,\ldots,\gamma_K \) respectively.
\[ F(X_i) = P(I \leq i), \quad i = 1, 2, \ldots, K \]

Here the probability \( \alpha \) refers to the chance that a bond stays unbroken and \( (1 - \alpha) \) infers the opposite. This bond selection procedure can be applied in various ways. For example, in place of finding a bond location for a chosen chain length, the above algorithm can be used for generating a chain fragment \( I \). Then deducting \( \ell \)th oligomers from the parent \( X \) chain, the remainder fragment can be obtained. In order to keep stringent record of the birth of all the daughter chain sizes and respective numbers, evolving in every new successive generation, it is necessary to keep track of both fragment sizes following a scission event. It is also assumed in the simple models that the occurrence of the latter at any instant will only yield two fragment chains. This means a chosen chain ready to degrade, can be split only in two and probability of splitting more than one bond is negligible. This assumption is maintained for the ease and accuracy of calculating the total molecules and total bonds that are needed for recurrent calculation of probability masses for certain non-iterative mathematical calculation processes discussed in chapter 5.

Alternatively, the algorithm can be used for generating two random fragments (say \( I_1 \) and \( I_2 \)) by repeating steps 6-9 twice. Combining the two gives the source length.

\[ : (I_1 + I_2) \approx X, \quad \forall \ X < N, \text{where } N = \text{largest size in a chosen interval}. \]

The above algorithm presents a reverse approach to the previous one used for selection and fragmentation of a polymer chain from the sea of molecules. This opens up wider scope to investigate various chain fragmentation mechanisms and possibilities of variation in product polymer MWD, evolved from the initial reactant polymer MWD. Comparison of the moments and averaging values between the two would be possible.

The algorithm is efficient for generating \( x \)-mer fragments for chains of higher MW, if implemented appropriately. However, due to its very random nature fragment sizes cannot be pre-selected and it disguises the actual scission
mechanisms. A further modification of this algorithm was used to compose a separate degradation model, which will be cited in chapter 5. A few other variations to the algorithms, discussed for non-uniform random number generation routines were tried. But the very discontinuous nature of probability manipulation over the whole range of chain population enforced some other kind of interference, causing interruption in maintaining the continuity in the curve contour. This was overcome with the help of the curve smoothing algorithm which was required both to compensate for any apparent disparity or divergence in the plotting co-ordinate data. An efficient smoothing algorithm has been investigated and 'Cubic Cspline' was found most suited to operate on a large number of data as in the current simulation exercise. This will be discussed next.

3.4.3. Introduction of Smoothing Routine
(Fig. 3.7- Fig. 3.15 & Fig. 3.16)

Results of any kind of experimentation need to be accurately validated, plotted and presented in a clear and meaningful manner. Likewise, the software output illustrates how good a model design is and what it signifies. In the present case, these are presented in the form of graphics - series of two-dimensional curves. An efficient curve optimising, smoothing algorithm- 'Cubic Cspline' has been achieved and implemented in the new model. The details of implementation and mathematical background is given in chapter 4, the results are shown in the next section.

3.4.3.1. Accuracy of Information

Why curve smoothing is necessary can be illustrated in terms of few example graphs (Fig. 3.7-3.15). MWD chromatographic plot presents a statistical overall view of the degradation state with respect to the entire polymer molecular population taking part in the reaction with the progress of time.
Initial Development Phase 3: MWD Curve Enhancement by ‘Cubic CSpline’ Smoothing routine Example 1

**Fig. 3.7:** Unsmoothed plot of “Randomcycle” MWD

**Fig. 3.8:** Averaged line smoothed plot of “Randomcycle” MWD

**Fig. 3.9:** ‘Cubic CSpline’ smoothing of “Randomcycle” MWD
Initial Development Phase 3: MWD Curve Enhancement by ‘Cubic CSpline’ Smoothing routine Example 2

![Graph of CutInHalf MWD](image)

**Fig. 3.10: Unsmoothed plot of “CutInHalf” MWD**

![Graph of Averaged line smoothed plot](image)

**Fig. 3.11: Averaged line smoothed plot of “CutInHalf” MWD**

![Graph of Cubic CSpline smoothing](image)

**Fig. 3.12: ‘Cubic CSpline’ smoothing of “CutInHalf” MWD**
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Initial Development Phase 3: MWD Curve Enhancement by ‘Cubic CSpline’ Smoothing routine Example 3

Fig. 3.13: Unsmoothed plot of “New Unzip” MWD

Fig. 3.14: Averaged line smoothed plot of “New Unzip” MWD

Fig. 3.15: ‘Cubic CSpline’ smoothing of “New Unzip” MWD
These graphical surveys also specifically provide information on the polymer structural issue. Polydisperse polymers are usually composed of intricate orders and levels of structural schemes. The resultant degradation behaviour depends on the latter as the ordered orientation started to be disrupted in gradual progressive steps. Thus clarity in plotting MWD curve shapes is important, as each helps in interpreting the temporal state of reaction and regional progress. Since the Monte Carlo simulation method involves large numbers of random repetitive phenomena the ultimate calculation causes severe irregularity in curve geometry. This leads to obscurity and misleading interpretation. To maintain the accurate curvature is not an easy task.

There are various types of interpolation methods and algorithms. Cubic-spline algorithm has been used and implemented here. This has been found to be easiest and most ideal in tackling the present problem. The power and sophistication of this method compared with the other two are cited in a few examples (Fig. 3.7 -- 3.15).

3.4.3.2. Accuracy of Plotting

The first set (Fig. 3.7-3.9) of example shows how irregular uneven edges of the MWD curves being removed by using the polynomial (cubic) Cspline algorithm. The second set (Fig. 3.10-3.12) shows how the same algorithm helps removing obscurities due to overlapping edges. The third set (Fig. 3.13-3.15) shows how polynomial interpolation of the graphic coordinates can be extended over a large area to recover the actual form and direction of the curve from its longitudinal divergence of data points which fluctuate within large amplitudes.

The operation of the use of these smoothing attributes -- i.e non-smoothing or rough appearance or average smoothing or complete refined smoothing can be chosen from the main window interface menu. Either one of the items can be chosen at a time. For refined smoothing (i.e. Cspline), there is an index parameter, which is a real number that controls the extent of
Initial Development Phase 3: presents smoothing index interface that provides a parameter for choosing the degree of refinement by Cubic Spline.
smoothing. This can be altered to high and low value depending on what degree of interpolation or smoothness is required. The interface with this menu is presented in Fig 3.16.

3.4.4. Improvement to Preferential Algorithm

A quasi-random number generation algorithm was next tried to replace the process of pre-selection of rectangular strips from the whole. The latter would enforce differential priorities among the molecular regions to participate in the decay reaction. The total molecules were divided into only two portions having the peak as the mean central position. Once this was determined together with the starting and end co-ordinates of the initial or previous distribution of the participant molecules, codes to implement a selection algorithm become much easier. Two random numbers are generated from both regions – high and low MW, using a composition method at each inner cycle. Each random number has its own density function and each variable occupies the respective rectangle under the density curve, where it is uniformly distributed. In this algorithm, it is assumed that, at any instant, the probability of chain breakdown events can initiate both simultaneously. The algorithm follows:

1. Find a, b and c where a represents the lowest size, c is the highest and b is the X-co-ordinate where size population takes a peak.

2. Associate probability masses for each point index in both the intervals (a,b) and (b,c) such that any random points l1 and l2, selected from each interval, can take a value 1 with probability \( \alpha_1 \), 2 with probability \( \alpha_2 \) .......K with probability \( \alpha_k \).

3. Construct probability density functions \( f_1(x), f_2(x), f_3(x), \ldots, f_l(x) \) for both intervals, such that the total probability density function can be transformed to one composed of a linear combination

\[
f(x) = \alpha_1 f_1(x) + \alpha_2 f_2(x) + \alpha_3 f_3(x) + \ldots + \alpha_k f_k(x).
\]
4. Generate a random variable from the total with probability density function \( f_1(x) \) in the interval \((a,b)\)

5. Find its index \(I_1\) from the transformed density function equation

6. Repeat step 4 and 5 for the interval \((b,c)\) and find index \(I_2\)

7. \(I_1\) and \(I_2\) are thus selected to present the initiation zones for an attack to be performed

8. Select the actual location of bonds where the attack will be realised, using any of the degradation models.

9. Extent of reaction, nature of cut, number of bonds to be split, what fraction to be recorded and what to be discarded are now determined by a subroutine

This algorithm was found to create many different ways of experimentation and helps to simulate various features of a complex reaction. Composite distribution that is made of arbitrary density components as height / depth and probability units \(\alpha_k\)'s, can be defined as respective areas partitioned by different sized rectangles. So the probability density with more depth will earn priority at the time of random selection. This idea was the basis for designing a network strategy of these reformed models. Computer interface strategies were used to create such a network and are called Slider I and Slider II. Their interface designs are discussed in chapter 5. Slider I will be discussed here with examples of its output. Slider II involves a continuous composition of probability functions and will be discussed in chapter 4.

3.4.5. Model Network Scheme

3.4.5.1. Slider Model I

This model allows the user to incorporate the different bond cleaving mechanisms simultaneously in a semi-random order using weighted probability. The algorithm could be a Monte Carlo probability simulation. A randomly selected molecule from the whole polymer system can be subjected to scission either at the middle of the chain or at weaklinks or any accessible stronger links. Otherwise it is chopped at a fixed length or
percent of length or unzipped from an end of the chain at each turn of time cycles. Slider 1 will weigh out the chances of occurrences of individual chosen scission modes by statistical calculation and exert this probability rating on the random selection from the total number of mechanisms each time. For example if the user set probability rating say 100 for 'Cutlnhalf' degradation mechanism, 50 for 'Weaklink' and 10 for 'Unzip'. These will be processed mathematically in such way that the chances of occurrence of 'Cutlnhalf' will be 90 times higher than 'Unzip' and 50 times higher than 'Weaklink' and so forth. Hence overall the chance of 'Cutlnhalf' mode of chain scission will be highest, that of 'Weaklink' will be next highest while chances of 'Unzip' occurrences will have the lowest profile. In outline the flow chart is: -

Step 1. Attach probability P to a scission mechanism M

\[ P_1(M_1), P_2(M_2), P_3(M_3), \ldots \ldots , P_N(M_N) \]

Step 2. Save the rates into an array

Step 3. Sum up => \( S = P_1 \cdot W_1 + P_2 \cdot W_2 + P_3 \cdot W_3 + \ldots \ldots + P_N \cdot W_N \)

Step 4. Generate a random number \( r \) => compare \( r \) with each of \( P_N \cdot W_N / S \) [ \( N = 1,2,3,\ldots , N \) ] until the value of \( r \) exceeds any of the above fraction

Step 5. That particular rank value will call the corresponding \( M_N \) [ \( N = 1,2,3,\ldots , N \) ] i.e. scission mechanism for execution for that particular time cycle.

Step 6. Select degradation area or strip from the total polymer composition as described in previous sections, in summery:

\[
P_{S_i \rightarrow A \theta}(a,k) = \frac{\alpha_{S_i} \cdot F(X_{S_i})}{\sum_{j=1}^{n} \alpha_{S_j} \cdot F(X_{S_j})}
\]

\[
P_{S_j \rightarrow A \theta}(k,c) = \frac{\alpha_{S_j} \cdot F(X_{S_j})}{\sum_{j=1}^{c} \alpha_{S_j} \cdot F(X_{S_j})}
\]

Chain selection from different sizes:

\[
\text{Prob} \gamma_r = \frac{\gamma_r \cdot n_r \cdot (r-1)}{\sum_{r=1}^{c} \gamma_r \cdot n_r \cdot (r-1)}
\]
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Where \( \gamma_r \approx \#P^r_{s_r-i,k} \); \( n_r = \text{number of chains of size } r \)

Step 7. A bond selection from chain of size \( r \):

\[
\text{Prob}_b = \frac{1}{(r-1)}
\]

The above will be repeated until the final time cycle is completed. Thus this model allows expansion and integration of the other models as well as giving option of combining / mixing any number of models as desired for each separate model run and thus amplify the scope for simulation experimentation using the iterative method. A flowchart of this model is given in Fig. 3.17 and the results in Fig. 3.18-Fig. 3.24.

3.4.5.2. Assumption for the model

The system reactor consists of several types of reactant polymer zonal aggregates \( S_i \) with probability masses \( \alpha_i \) and density functions \( F(X_i) \). The intervals \( (i,k) \) are considered as active centres, reacting with one or more chains to yield the polymer chain fragments of smaller sizes. The reaction mainly propagates in order of priorities with probability weighting \( \gamma_s \) in the zones \( S_r \) and according to the bond densities in that location. An arbitrary quantity \( \Phi_{S_r} \) is used to make random estimates for the extent of reaction between two consecutive inner time cycle instants as well as two outer time segments. Invasive scission is considered negligible at the very low MW end during the initial period of reaction propagation due to inertness of the amorphous region to thermal attack on a complex polymer like Cellulose.

The reaction propagates slowly in the low MW region after the large molecular aggregates \( S_r \) in the high MW region are exhausted. The quantity \( \Phi_{S_r} \) indicates the remaining reactive chains in the system likely to be cleaved, at the end of each outer time loop. This controls the extent of reaction propagation in the subsequent time intervals. The rate constants between different molecular aggregates do not remain constant, but vary from zone to zone as well as from one time segment to next, such that:
The above processes have been repeated many times in order to obtain the required averages of molecular weight (i.e. $M_w, M_n$ etc.), the molecular weight distribution $W(n)$ and the dispersity $d = \frac{M_w}{M_n}$.

$P_{SI-AB} (a, i)$ and $P_{SI-BS} (j, c)$ satisfy:

$$\sum_{i<j} |P_{s_i-AB} (a, i) + P_{s_j-BC} (j, c)| = 1$$

Equation (18) was assumed to be comprised of the individual following domains of the uniform population of distributed random numbers between $[0, 1]$ and the probability of the above numbers of events would be adjusted in the computer set up depending on the domain the number belonged to:

3.4.5.3. **Description of Flowchart (Fig. 3.17)**

The above flowchart (Fig. 3.17) describes an ideal implementation of Monte Carlo dynamic method that is structured with several levels of probability density functions. The latter was necessary to control the creation and spread of a degradation zone in the context of more than one scission event operation strategy. Creation of a new degradation zone per unit time-slice replaced the elaborate repeating nature of single chain breaking per unit time-cycle of the initial algorithm (Fig. 3.3b). In the place of a single scission event a cluster of events may occur in the form of geometric progression keeping abreast with the ultimate end effect resulted from the summation of
Initial Development Phase 3: Introduction of Monte Carlo Probabilistic Model Network and Algorithm Flow Chart

Fig. 3.17: Presents a flow chart of improved probabilistic model implementing a event-network of scission models (Slider I)
huge number of unit time sequences. This yielded better results to observe the effects from a singular reaction strategy to the possibility of simultaneous occurrences of multiple reactions in a polymer matrix. The structure of the algorithm can be compared to that of Schiuchuk and Lutsyak (1993), who attempted a stochastic MC model in Fortran-S to deduce the intermediate changes in MWD. However the application of probability functions are quite different. The \( W(r_j) \) function defining the event-ranking operation is described in section 3.4.5.1. The \( P(r_j) \)'s were derived from equation 22-24 described in section 5.4.3.2.1 in chapter 5. The concept of evolving degraded micro-zones in place of a unit reaction spot can be compared to Rapoport and Efros (1995) MC model. The latter recorded the number of micro-cracks leading to 'Percolation Cluster' in order to define ultimate system failure in thermo-oxidation of solid polymers. Thus the algorithm incorporated more flexibility and speed to the simulation of a large variety of polymer degradation system that varies from one to another in their inherent multiple reaction strategies. The ultimate state change behaviour of this algorithm can be analogous to the one adopted by Huang et al. (1995) that interprets the entire system trajectory in terms of Markovian N-dimensional Walk of molecular population of N different species. The results of this model are given in the next section.

3.5. Simulation Results of Improved Model
(Fig. 3.18-3.24 & Fig. 3.25)

Some examples of the single simple models are displayed to show how different models vary in their individual unique shift pattern (Figures 3.18 – 3.22). Examples of 'Slider I' model network outputs are displayed next with both normal (Fig. 3.23a-f) and skew (Fig. 3.24a-f) initial distribution. Both models display their dependence on various degradation parameters such as percent and length to be cut from the end, weak-link interval, the shape and broadness of the initial distribution. In addition, the number of unit-inner cycles and their individual intervals, the number of outer time-cycles, that dictate the time duration of degradation, the probability weighting and control
on the preferential degradation of the polymer chain subsets etc. are input variables. In model networks, the extent of these variations increases with the number of single models participating. The curve shift and shape patterns are also changed radically with the variation of the percentages of the individual models as shown in Figures 3.23 and 3.24. More details of the 'Slider I' interface are given in chapter 4 with a brief description of how various controls and variables work in this model.

**Effect of 'CutinHalf' (Fig. 3.18a-d):** Simulation examples display a multimodal MWD trend that is unique to this type of scission due to each length category yielding individual peak at positions of half their sizes.

**Effect of 'Weaklink' (Figure 3.19a-h):** (a) Normal Initial Distribution (medium range), varying weaklink bond intervals from smaller (500) to larger (1200) decreases the broadness of bimodal intermediate peaks. (b) MWD patterns with cellulose sample 146 as the initial distribution, longer degradation cycles and a fixed weaklink interval (900) shows a gradual peak broadening with height-loss, characteristic of intermediate cellulose degradation.

**Effect of 'Unzip' (Fig. 3.20a-h):** (a) The longest chain cleavage was given priority in this algorithm and the smaller fragments assumed volatile. This minimises lower end scatters as indicated in the other figures. (b) The model exhibits the following features with smooth gradual peak movement towards lower MW:

1. Flattening and broadening of peak progression typical of cellulose and chitosan (see GPC Figures 2.8a-d and Fig. 2.9a-c in Chapter 2).
2. The broader the initial distribution the lower the intermediate Peak height losses as the degradation cycles increase.
3. The latter also displays a distinct peak sharpening and height raising effect at the lower DP.
Initial Development Phase 4: Examples of Multi-modal MWD Curve Trend with 'Cut-in-half' Scission

Fig. 3.18a-d: show subsequent peak appears exactly at the mid-point of its preceding ones- (a) random sampling with concentric inwardly reducing curves, (b-c) narrower the initial distribution less defined the degraded peaks tending to baseline scatter, (d) broader the initial distribution more well defined the successive product peaks.
Initial Development Phase 4: Dependence of MWD Trends on Simulation Attributes (single scission mode - ‘Weaklink’)

Figures 3.19a-h: display different trends (a-d) by altering ‘Weak-link intervals (a) 500, (b) 900, (c) 1000, (d) 1200; (e-h) changing number of inner-cycles (e) 200, (f) 300, (g) 200, (h) 300; changing initial distribution (a-d) Normal and (e-h) Gamma / Gaussian.
Initial Development Phase 4: Examples of Smooth Gradual MWD Shift with Unzip

Figures 3.20a-h: show MWD trends for 'Unzip' model exhibiting (a-f) smooth gradual peak movement towards LMW region without any base line scatter using either of (a-d) broader and (e-f) sharper initial distribution with variable outer time-cycles, (g-h) scatter of generated fragments at LMW due to partial unzip.
Figures 3.21a-f: show (a-d) MWD curve trends switching from initial unimodal to bimodal and trimodal peaks with the advancement of decay- (a-d) ‘CutFixedLength’ and (e-f) ‘CutFixedPercent’, yielding more well defined peak and curve shapes without any fragment accumulation at the LMW region as seen in the former curves (a-b).
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Initial Development Phase 4: Examples of Bimodal shapes using a 20% endcut and Initial Gamma Distribution

Figures 3.22a-h: display MWD curve trend variability in 'CutFixedPercent' scission model with different percent endcut and inner time-cycle intervals, the initial distribution remaining the same. Note emergence of a bimodal pattern with 20% cut in (c-h).
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Initial Development Phase 4: Examples of the Results from Model Network (Slider I – combination of scission modes)

Figures 3.23a-f: show results (a-d) of mixed scission modes combining different sequences of random scissions, Note: excessive scatter at LMW region in (a-b) due to more occurrences of 'CutinHalf' and less 'Unzip', (c-d) Using more 'Unzip' cut down the scatter, (e-f) change to preferential scission, superimposed with a lab-experimental data set of decay of Cotton Linters (Oil, 120°C).
Initial Development Phase 4: Examples of MWD Curve Shift Patterns using a Skew Initial Distribution

Figures 3.24a-f: show MWD curve shift patterns of (a-d) 'Slider I' 'MixedModes' and (e-f) single scission models e.g. (e) 'Weaklink' and (f) 'Unzip' with a 'Skew' initial distribution where the emerged patterns display dependence on scission attributes, time distribution (time-cycles) same as its 'Normal' counterpart.
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Effect of end-cut e.g. ‘CutFixedLength’ (Figures 3.21a-f) and ‘CutFixedPercent’ (Figures 3.22a-h): Show contrasting features such as bi or tri modality displayed by these two end-cut mechanisms through the computer simulation degraded resultant MWD curves. The former chops away a predetermined equal length from ends of polydisperse material at each degradation cycle. The latter chops equal percentage of the original initial length for each chain length sizes. The basis of both models is quite similar. The examples show the curve shape variation by varying different degradation parameters and initial distribution attributes. ‘CutFixedPercent’ model is of most interest, as this mechanism is more generally applicable to most polymer chain scission strategies, where any percentage from the end can be fragmented. The shift patterns of the single model application of these scission modes seems to be common among the synthetic polyolefins and similar linear or branched polymer radical or thermal oxidation, exemplified in Fig. 3.25a-d. The latter presents lab-derived MWD from GPC. The unimodal sideway shifts without the loss in height exhibited by the top figure of Fig. 3.25a, which reflect the similarity of the simulated ‘CutFixedLength’ that is fully biased to the scission of only the longest chains. The bottom figure of Fig. 3.25a resembles a mixed model combining ‘Unzip’ and ‘CutFixedPercent’ modes that ultimately transform unimodal MWD to a bimodal one. Fig. 3.25d GPC of polyethylene degradation can be interpreted by the same reasoning whereas Figures 3.25b and c display a very simple pattern to a shift of single random scission.

These simulation graph-analyses show –

- Random models display mono-modal MWD curve patterns, meaning various polymer molecular segments are equally accessible for degradation.
- Nonrandom models shows complex patterns with bimodal or tri-modal features or irregular broad curve peak shape in contrast to the usual smooth sharpness. This conversion from mono-modal to multi-modal feature primarily reflects the diversity of chemical kinetics i.e. absence of a unique kinetic order or rather existence of multiple reaction rates, that can
Decay Pattern of other Polymers (linear/branched) obtained from GPC

Fig. 3.25a-d: Shows dependence of MWD curves deformity pattern on initial distribution and environment enforcing gradual progress of decay of (a) SKS30, (b) Polypropylene, (c) PCT1 and (d) Polyethylene. Note all display lateral curve shifts to lower molecular weight curve with reducing shoulder/tail at high molecular weight end those are unique to individual polymer architecture.
be attributed to different molecular sub-populations or subsets from the entire region taking active participation. Note peak broadening tends to extend towards LMW, with a bimodal shape as the reaction proceeds (Figure 3.22a-h).

**Effect of Slider I combining the above single models (Fig. 3.23a-f- Fig. 3.24a-f):** Model shows emergence of a well defined bimodal peak at initial phase superseded by a peak broadening starting at some intermediate stage. The algorithm leads to a smooth even spread of newly generated molecules of intermediate lengths as the percent of 'Unzip' increases and 'CuinHalf' decreases. These features are uniquely displayed by Cellulose during at 120°C (see Fig. 2.8a-d). The model reproduces the experimental peak attributes of the data reasonably well. Former figures used Gaussian /Gamma and the later used a skew initial distribution.
3.6. Conclusions

- Initial optimisation of Simulated MWD curve features were achieved by introducing a colour palette and an efficient smoothing routine called 'Cubic Cspline'.

- Lateral shifts in the subsequent temporal curves from HMW to LMW as observed in GPC derived curves, were achieved by implementing a set of non-uniform probability weighted functions, that enabled the incorporation of preferential manipulation of scission in the longest chain domains.

- The Monte Carlo dynamic method was then adopted and the algorithm was further expanded to execute a strategy of multiple scission events or creation of scission zones for a longer time-slice instead of unit time-cycle, distributed in micro-scale. This incorporation was made easy and simple to operate through designing and implementing the Slider I interface. The flowchart of the latter is given in Fig. 3.17.

- The results (Fig. 3.18-Fig. 3.24) illustrate the smoothed MWD curves and their clear images with desired lateral shifts towards LHS. The figures also show the dependence of the resultant temporal curves on the variables such as scission attributes, initial distribution, the broadness of the latter, the length and extent of the time distribution of decay etc.

- The simulated MWD curves show the extent of lower molecular weight scatter also depends greatly on the nature of the scission whether preferential or random. For example more scatter appeared in the 'Weaklink' or 'Cutfixedlength' scissions than 'Cutpercent' and 'Unzip'.

- Combining scission modes yielded more interesting MWD curve patterns. For example, a combination of 'Unzip' and 'Weaklink' generated a bimodal trend whereas 'Cutinhalf' generated a multimodal trend.

- Preferential attack by the degrading agents (e.g. heat, acid, moisture, oxygen, impurities) at the longest chains, following an initial short phase displayed by the above results are characteristic of complex macromolecular substrates like cellulose, chitosan, multi-stranded polysaccharides. This feature will be further examined in logarithmic scale in later chapters.
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- The clarity and the accuracy in generating the molecular distribution curves is important in order to describe explicitly the temporal behaviour of decay progression in terms of polymer compositional changes as reflected by simulated MWD curves.
- Above examples of simulation model graphs and their comparative study on a cellulose sample (cotton linters 146 set) show the following:

1. Any of the single model mechanisms of "Cut in half", "Weaklink" or "Unzip" alone is inadequate to reproduce the MWD pattern.
2. Model "Unzip" seems to be the closest, if combined with "Weaklink" mode in the initial stages of degradation.
3. Preferential scission mechanism model the sample MWD peak shapes and curve patterns as they shift from HMW (up) to LMW (down) field, better than their random counterparts.
4. Thus preferential models based on "CutFixedPercent" successfully displayed many of the features of the experimental data set.
5. This simulation study also favours preferential scission of higher molecular weight chains (in crystalline regions) or the longest molecular subsets to lower molecular weight ones, which contradicts the chain cleavage theory suggested by Cosgrove et al (1985) and supports the postulation of Emsley (1994, 1995) and Viebke et al. (1994).
6. More detailed simulation study shows that thermo-chemical or thermal modes of attacks dominate the other competitive degradation processes. As such, the initial rate of chain cleavage is more likely to be proportional to the mass frequencies or weight fractions of different chain lengths present in the initial distribution.
7. However this changes in the intermediate stages of degradation, when probability density is more weighted towards the high molecular weight subsets. This is the time when a build up of a wide range of newly generated fragment chain occurs, which, together with original LMW undegraded chains, gives flattened, broad (sometimes irregular or bimodal) peak-shapes for different cellulose samples.
(8) It should be possible to prove from the simulation experimentation that the rate of chain scission is independent of the weight fractions or concentrations of individual chain length, but is proportional to the extent of molecular chain lengths. This is featured in bimodal curve shape generation during the intermediate degradation phase—a shift from initial mono-modality. Thus MWD curves clearly portray deviation from a general trend of kinetic linearity to non-linearity, as a resultant of multiple scission rates.

(9) Simulation experiments with varying parameter values further indicate thermal dependence of the changes in peak attributes. The reactivity of different regional chain segments is controlled by the temperature differences in the similar manner as it controls the extent of molecular events and kinetic parameters.
Chapter 4

Software Design and Implementation

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4.1. Introduction

The use of object oriented programming (OOP) language to construct the software to simulate complex polymer degradation is described in this section. The program serves as the main body of the vital instrument working behind the entire simulation operation process. The MFC Visual C++ programming platform (Microsoft) is used for development of this OOP program. The developed program provides the functionality needed to fulfill the demands of simulation experimentation as well as to emulate the more complex nature of degradation strategies. It caters for multiple results outputs, in the form of separate window interfaces and provides an important tool to complement otherwise time-consuming laboratory studies. The program consists of 9 main modules (classes), 386 sub-modules and some 4000-4500 lines of code.

An OOP program consists of a structured series of modules, sub-routines, functions and individual instructions, written in a high level language (C++), compiled and linked together into an executable program in machine code. The mathematical components of the program describing the degradation models are called algorithms. The aim of modern window based programming is to make the program parts more accessible to the user or researcher via interface message passing. This trend has been followed in designing the present program development. The implementation of the algorithms can be comparable to the writing of protocols in order to conduct a lab-based experiment.

One of the most important achievements in the construction and design of the current modelling software has been to optimise the program with sufficient flexibility to predict and generate the likely behaviour of a real system. This requires close interaction between the user front and computer operational environment. The incorporation of series of "Interfaces" helps the user to step into, communicate with and manipulate the computer. A brief discussion of the program design aspects and interface layouts are
detailed in this chapter and an exemplar program executable file with operating instructions is included in Appendix 4. The program code will be found in the attached CD with file archives of program output.

4.2. Program Infrastructure (Fig. 4.1- 4.2)

Windows based software comprises three main structural elements—user Interfaces, document-template document-view template and view output at the user front. A set of various data values for the parameters is indispensable to run a simulation experiment. The user can input values for all the simulation parameters via the front end user interfaces. There are various types of interfaces, varying in design and implementation within the software. The most popular is ‘dialogue box’ or ‘list box’. Each interface is designed and drawn with the aid of the ‘App Studio’ utility, and configured with a set of control boxes and buttons, each of which are linked to a distinct ‘class’ and their own data storage variables, called attributes. The control boxes such as radio buttons, combo and edit-boxes etc. are embedded in the form of child windows in the template of the dialogue window to communicate with the user and receive user-input data. The variables distribute the flow of data-values to various programming objects and components (e.g. transformation models, mathematical equations, data transformation and filtering, generation of various graphical features). A brief concept of general design of software implementation is outlined in figure 4.1. The figure shows how user defined data flows through various intermediate data processing stages within the program architecture, undergoing transformations necessary to conform to desired outputs at the user output end. The latter displays simulation results and charts and so needs to be presented in multiple windows, for clarity and comparative study. Invalidating the window’s client area, which triggers the disappearance of the previous image and repainting it with new chosen plot from a window menu with generation of new image achieved this. The details of the various interfaces appearing at various stages (e.g. beginning, intermediate and output-end) or program-run are given in section 4.3.
Fig. 4.1: Basic Structural Design of Software
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Input data, inserted at the user front, are validated, collected and stored in a single document, created for each initial data entry stage. These are then efficiently dealt and packaged into suitable storage global data-types for further processing and calculation etc. The document's view objects mostly accomplish the action tasks. A central document organiser – 'Document template', creates each document. Each is presented by it's own 'View template' – organising single or multiple viewing outputs. These two main modules work in concert with the help of many subsidiary modules, functions and procedures. Many of these sub-modules are encapsulated in separate hidden independent individual program entities, called classes, to create a organised structure –the object oriented program (OOP). Fig. 4.2 presents a super-level design to show how two parent classes ('CpolydegDoc' and 'CpolydegView') were organised in the current program with encapsulating several such modules. While the related sub-modules or classes data member are responsible for packaging of groups of parameter values, the class member functions carry out the program commands for desired manipulation. The class objects preserve inherited characteristics or functions, which are kept hidden and are not visible to other program constituents in order to preserve their unique functionality. Only some of the 'friend classes' can share these features. This strategy avoids the risk of code alteration in subsequent versions of program during its developing stages. As the constructor creates a class object, it inherits automatically the class properties, which are exploited in manifesting optimised control and order to program module performance. For example, the 'curve smoothing' module only perform smoothing of curve contour and as such is very distinct from the 'Data reminder 'list box' Interface, that keeps a record of various parameter values input by user at the start of the program. When the user at the end of program run calls the latter, it displays the 'list box' containing collection of data values, attached to a particular graphical interface. The two modules perform two different jobs on the data objects as the latter deflect through various intermediate stages and belong to two separate classes. One cannot share the other's functionality. The 'View' class thus co-ordinates other classes and modules leading to an integrated output as shown in Fig. 4.2. Similarly other class's composition will be discussed next.
Figure 4.2: Class Implementation Architecture Design
4.2.1. Class Infrastructure (Fig. 4.3)

MFC Visual C++, provides a platform for object oriented programming (OOP) language, which encapsulates a program element in such a way so that its code can be kept hidden and reused many times by the other modules or program. This renders clean, tidy and bold structuring of codes. Reuse of codes thus avoids bulky coding and increases processing speed. Invisibility of codes prevents accidental alteration or muddling of codes in the course of program development. OOP involves most sophisticated but difficult programming methodology. Fig. 4.3 shows how the various program operations, shown in Fig. 4.2 are encapsulated in a class oriented structure, implemented with separate identity. Each class has a class’s header (*.h*) files, which interfaces the class declaration of its member functions and data components with the '*.cpp’ files, which hold the implementation of its functions. Classes manifest different functions and can work individually or be used by other classes. For example, 'Ctex' and 'Cdegrad' classes package the data of co-ordinates into a pointer array and manipulates this array to enable the plotting functions to plot the co-ordinates within the window client area. These Classes are embedded in 'Document class’ but are used by 'View class’ for plotting. Class 'CPolydegdlg' receives data from the 'Data-entry’ interface and package these data into suitable global form for their further processing. 'CExppar' class deals with processing experimental and any externally pre-saved data and is only connected to the 'experimental’ interface. 'CPolydegView’ class calls classes like 'CPolydegReminder’, 'CPolyPVVal’, 'CPolydegProgress’ and others to perform their individual unique functions by respective subroutines.

4.2.2. Class-Interface Foundation

Fig. 4.3 outlines a flavour of clear-cut style of OOP implementation technique. The latter enable derivation of both inherited and non-inherited ‘Classes’ to feature all the utilities of “Interfaces” in the forefront. One ‘Interface’ may be attached to a single class or a number of “Classes” may be attached to a single 'Interface’ or a big ‘Class’. The other important
Figure 4.3: Object Oriented Design Of Interfaces

[Diagram showing object-oriented design with various classes and interfaces, including:
- Class CPolydeg
- Interface 1 (Data Entry Dialogue Box)
- Interface 2 (Exp. data Processing Module)
- Interface 3 (Monte Carlo Random Model Processing Slider I Module)
- Interface 4 (Variable Kinetic Polymer Subset PDF Model Processing Slider II Module)
- Interface 5 (Data chart Processing Output Module)
- Interface 6 (Time Progress Bar Display Module)
- Class CpolydegView
- MWD Curve-Output Processing, Graphic Plotting Module
- Class CpolydegDoc
- Preparation of Document - data storing, validating & packaging Module]
feature of OOP is the creation of ‘Document’ and ‘View’ Class templates. The latter become the birth origin of many instances of ‘Document’ and ‘View’ objects, generating several cycles of a model run and separate resultant displays. Many different types of model can be run in one execution, without having to re-build or re-compile the program. Principle ‘Interfaces’ will be introduced and discussed in next section.

4.3. Interface Module Operation

An interface in computer software represents a visible layer with a window style appearance in order to mediate exterior communication between user and computer. A number of appropriate attributes or parameters are presented in the form of various resources symbolic designs, called “controls” labelled with their individual text (names). These can be suitably laid out in orderly dimension by the aid of “App studio” on usually a dialog type window front. There are different categories of window design depending on their use. However, the main purpose of designing separate interfaces to perform distinct operations is to enable the end user to feed data and values to the parameters to carry out large-scale experimentation with ease and convenience and control program output. A few interface windows are briefly described below.

4.3.1. Description of the Main Interfaces

4.3.1.1. Menu Interface (Fig. 4.4 - 4.7)
This is the main parent window interface with the top headings such as ‘File’, ‘View’, ‘PDModel’, etc. as shown in Figure 4.4(a). Figure 4.5(a-c) – displays the entire sequential ‘Main-frame Window’ menus and submenus. For instance ‘PDModel’ contains two submenus – ‘Data Entry’ and ‘Experimental’. The prompts the parent window to create a dialogue box object of ‘data-entry’ type, which appears on the template of the main window with an initialised, set of data values on it. The User can input, change and/or select the desired data by altering some of the initialised values. The second submenu creates a dialogue box object of ‘Expper’ type
Examples of Program ‘Polydeg’ Mainframe Window Interface Menu and Submenu Branching

Figure 4.4: displays various Menus-submenus branching (a) on the template of Mainframe Window Interface, e.g. (b), (c) and (d) shows various submenus of ‘Graphics’ Menu in pull-down style, those with a side arrow display their individual pull-down style submenus on the RHS, for example a submenu ‘Polydispersity + Reaction rate related’ has two subsequent levels of submenu etc., in contrast to the large Menu, (e) bottom displays a short menu ‘PDModel’, consists of only two items – ‘Data Entry’ and ‘Experimental’.
Examples of Individual Menu Items

Figure 4.5: displays a serial arrangement of individual Menu and their related Submenu and items they include e.g. (a) ‘File’ submenus list (topmost LHS), (b) same for ‘View’, (c) ‘PDModel’ submenus, (d) ‘Graphics’ submenus list and the same for one of its submenu ‘Distribution’, (e) ‘Window’ submenus list – (a), (b), (c), (d) and (e) are placed next to each other downward.
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to accept experimental MWD data from a file. These dialogue boxes are
called child windows and each of them is composed of separate individual
interfaces to conduct data values and other commands from the user to the
program modules. However, not all submenus generate a dialogue window,
some are used to obey commands. For instance, the rest of the figures
(Fig. 4.4 – 4.6) display various submenus and their extensions from the
‘Graph’ menu (Fig. 4.4 b-d) and are used to create different graphical
interface output from model runs. ‘Run Model’ initiates a model calculation
and displays a ‘Progress Bar’, until a simulation model run is complete, after
which the user can select from various graphical submenus to examine the
simulation output. Note that also until the model run is complete, the ‘Graph’
(Fig. 4.5d) and ‘Chart’ (Fig. 4.6f) submenus are displayed in grey, indicating
their operations are not accessible. This is to caution the user that no
simulation experiment has been done and hence the transformed resultant
data required to produce the graphics etc. are not available. A similar
strategy is adopted where the action of a submenu is dependent on the
selection and performance of the other and hence need to be selected in
succession.

The ‘DP averages vs. Time Plot’ submenu of the ‘Graphics’ menu produces
two different views of the decrease in average degree polymerisation with
time graphs, depending whether ‘DPn’ or ‘DPw’ is selected, as shown in
Fig. 4.4(b). The latter also displays ‘Polydispersity + Rate related’ submenus
(Fig. 4.4c), which presents a choice of three further submenus – ‘Scission
Extent per cycle’, ‘Turnover Extent per cycle’ and ‘Theta Measure per cycle’.
Each of the latter has three more extension submenus – ‘Second’, ‘Minute’
and ‘Hour’. The latter items are the end in the series of the submenu
selection and when clicked will generate a time graph graded in their
respective time units. The detailed output of these various graphs will be
presented in Chapter 6.

Figure 4.5 (a-e) displays the submenus of subsequent menus. ‘File’ has the
usual submenu such as ‘Save’, ‘Open’, ‘New’, ‘Exit’ etc. as in ‘Word’
software. However, ‘Save ndata as’ ‘Save bitmap as’ are new
Figure 4.6 a-f: displays more details of (a-d) 'Graphic' and (e-f) 'Chart' submenus. Note some of the submenus are displayed in grey (f) i.e. disabled for view, these will be enabled automatically at different stages of program-run,
implementations and are called to output save in an external file in a format such as text, notepad or a particular image format. ‘New’ will call for the preparation of a new document, created by the ‘Polydeg Document’ class, so that the program can make a start on a new simulation experiment and receive new input data from the user interface port. Thus a large number of simulation experiments can be carried out in succession in multiple windows, as cited in figure 4.7 (a-b). Window’s ‘View’ submenu creates a ‘Cascade’ or ‘Tile’ display of a series of graphs or charts, as in figure 4.7(b). The graphs can be displayed from the ‘View’ submenu in ‘Superimposed’ view mode for close comparison, as shown in fig. 4.7(a). The multi-window design is very useful for simulation scenarios and comparative studies.

The status bar dictates precisely the use of each menu, submenu, or use of a dialog-box controls etc. It allows guide dialogue sentences to run through the status bar template. ‘Data Rendering’ is used to allow various manipulations of graphic output plots and interface details will be given later. ‘Distribution’ provides different selections of the main MWD time-related graphic output in either ‘Linear’ or ‘Log-Linear’ form. Fig. 4.6(f) shows that some of the ‘Chart’ menu items are inactive initially but in the next figure these have become active as the model run is done and the main ‘Distribution’ MWD time curves are generated. Fig. 4.7(a) shows three separate document windows with three separate sets of simulation results curves to compare. In the fig. 4.7(b) four different graphs and charts, obtained from a single simulation run, are opened in separate window interfaces for close examination.

4.3.1.2. Main Data Entry Dialogue-box (Fig. 4.8 a-f)
The interface is displayed in Fig. 4.8a-f. It serves as the primary data input stage, receiving values for several categories of parameters, such as scission model attributes, graph plotting attributes, mode of PDF selection, time calculation functions and display, mode of graphic display etc. The user must first complete this input stage in order to carry out the model run, as described next.
Example of Multiple View Window Interface

Figure 4.7: displays use of multiple ‘View’ window output at two separate program run. (a) shows three ‘View’ windows exhibiting three different simulation model-run MWD graphic, (b) shows four ‘View’ windows exhibiting three separate graphics and one chart – referring result output from the same model-run. This shows how multiple interface display implementation helps to carry out comparative study with the simulation experiment results.
4.3.1.2.1. Attributes of the Dialog Interface

Model: This combo-box is drawn and designed to contain a list of various scission model names (Fig. 4.8b). One can be selected for a model run. Choose Random by: is implemented to contain a list of 'Strings' (Fig. 4.8c) that distinguish what extent of randomness should be included in the PDF construct. The latter is defines the mode of chain and bond selection process per model run.

Distribution: This combo-box is designed to contain a list of 'Strings' (Fig. 4.8d), which refer to the type of initial (i.e. at zero time) molecular chain-length / weight and frequency distribution is used, such as Normal, Beta, Weibull, Experimental, Skew etc. The initial distribution refers to a pre-set distribution of the intact polymer molecular size population.

Choice of bond: This combo-box determines the bond location along the length of the molecule where scission occurs during each inner time-cycle. This could be by first choosing a molecule then a bond within the molecule or by choosing a bond and the identifying which molecule it is in. There is also option 'none' which is chosen for those models that are not dependent on the above two-selection mode.

Initial distribution parameters: presents a selection of distributions that includes initial distribution curve construction parameters. Also the sections with heading 'Weibull' and 'Beta' distribution includes edit boxes to receive user parameter values, in order to construct the shape of the initial distribution curves of 'Weibull' or 'Beta' type.

Scission Attributes: The middle section is associated with the parameters that control the scission actions that occur during a degradation run. In the case of non-iterative models, some of these only participate.

Total Pdcycles: this edit box takes integral input that specifies the total number of outer time-cycles permitted in the model run.

Choose Parameter variation: This section includes two radio buttons to indicate whether the run will be in (a) variable mode or (b) fixed mode. Variable mode allows the scission parameter values to vary each inner time cycle occurrence. Fixed mode keeps them fixed over the entire duration of model run. The variable mode includes some of the main parameters such as 'Cycle length', 'Weaklink Intervals', 'Percent Cut' and 'End Cut'. The
values of the latter can be pre-selected by the user, by entry into the respective edit-boxes, while the ‘PDCycle’ combo-box on the left of ‘Cycle length per cycle’ is set to display the corresponding outer time-cycle occurrence numbers (Fig. 4.8e).

*Cycle length per cycle:* takes integral values that signify the number of iterations of the inner time-cycles for each successive outer time-cycle during a model run.

*End Cut:* limits the program to generate a fragment of approximately fixed magnitude following a scission event. This magnitude may vary along the outer time-cycle orbits if the variable mode is switched on.

*Percent Cut:* same as above except a percentage fragment from the end of the selected molecule chain would be generated.

*Weaklink per cycle:* takes an integer value, commanding cut at defined intervals, if Weaklink mechanism is included in the model run. Dispersity cut about a mean: a value used as a standard deviation around every weaklink or other mechanistic cleavage point. This also helps to create some randomisation around a fixed given value in order to mimic reality in the simulation of a scission mechanism.

*Change of Intermediates:* a value in this edit-box controls the lower size limit of fragment intermediates to be recorded in the periodical distribution count and in the total molecules count. This value is randomised using a ‘rand( )’ function in order to fluctuate around a mean and standard deviation which may vary per cycle.

*Save Larger Fraction only:* This is a tick box that signals to the program to record only large fragments and to ignore the smaller ones generated from molecular scission events.

*Time Attributes:*

*Choose Time Function:* User can make a choice of either a Linear or Non-linear method of time calculation such as Poisson, Exponential etc. This combo-box retains a list of the latter for selection (Fig. 4.8f).

*Display Type:* a Combo-box, which keeps a list of ‘Strings’ of how the time can be displayed divided in the chosen units (e.g. day-hour-minute or year-month-days or simply in hours etc.).

*Initial Rate and Effector:* parameters used by linear time rate calculation.
Figures 4.8a-b: display (a) ‘Data Entry’ dialogue box user interface and its various control boxes (edit, combo), radio buttons for user to enter values for simulation parameters and attributes as well as commands, (b) shows Model Menu combo box containing a list of model menus to choose for a model-run.
Figures 4.8c-d: display (c) ‘Choose random by’ combo box contains a list of menus to choose that passes a command to the program to control the degree of randomness of bond scissions to be performed by a model-run as stipulated, (d) the combo box to choose the type of distribution for the initial MWD at time zero before decay starts in a model-run.
Figures 4.8e-f: display (e) ‘PDcycles’ combo box contains a list of numbers referring to time-cycles so that scission parameter values can be entered to other respective edit or combo boxes and varied for each selected cycle number, (f) ‘Time-function’ combo box to choose the type of time function to be used by the program run that determines the desired time distribution to be set for entire decay.
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Graphic parameters: This section enclosed under the heading of 'Scope of DP and 1/DP' includes various arbitrary parameters that are used to feed plotting routines.

The buttons on the extreme right hand side of the dialogue box:

Sliders: When clicked, brings the 'Slider I' dialogue box into view on the main window. This is used for the model network.

Reset Exppar: Clicking this button resets automatically the initialised data for each sections of data entry boxes, where initialised data values differ according to the state of the 'Exppar' flag variable values. The latter indicates if the laboratory experimental data is chosen to provide for the initial distribution or not and also what kind of output display is selected etc.. The initialised data values are different depending on what type of initial distribution is selected. This is linked to a function, which checks the 'Exppar' variable and resets the values of the parameters accordingly.

Save and Load: These buttons trigger the save files and load file from a list of files allowing the user to save the parameter values from the data entry box to a file or to load a pre saved file.

Rating Model: This button when pressed creates the 'Slider II' dialogue box interface, which is used to create more a complicated reaction system. More about the above interfaces will be given in next section.

4.3.1.3. Interfaces to Save and Load Files (Fig. 4.9-4.10 a-b)

Figure 4.9 (a) displays both the interface appearance and an example of the content of a saved '*.par' file. Each sample attributes for a simulation experiment is saved in a '*.par' files. Fig. 4.9(b) displays the way the attribute values are written in a text file and stored for future use. When, in future, this particular file is selected for loading, the values will be transferred to the respective parameter variables. Various control boxes that comprised the Data-entry dialogue box as shown in Fig. 4.10 (a-b) will display the latter. A window interface will appear when the Save button is pressed. Likewise an 'Open window' interface will appear with the saved files when the Load button is pressed to enable the user to select a '*.par' file to be loaded. Both operations are performed by separate program routines. The '
Interfaces for Data File-Save-Load & Input-data-Display

Figures 4.9a-b: display (a) saving operation of User ‘Data Entry’ dialogue box parameter values into the corresponding data-variables of ‘*.par’ file via ‘Save As’ interface that is called on pressing ‘Save’ button and similarly for loading previously saved ‘*.par’ file variable data values into the parameters of ‘Data Entry’ dialogue box via ‘Open’ interface on pressing ‘Load’ button in ‘Data Entry’ dialogue box, (b) exhibits two ‘sample.par’ file contents as example.
Examples of Data Loading from '*.Par' Files into Data Entry Dialogue Box

Figures 4.10a-b: ‘Data Entry’ dialogue box is loaded with the parameter values from (a) Sample10.par file, (b) from samp2.par file. Both the ‘.par’ files’ contents are displayed in the previous figures.
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OnSave Param ( )' routine reads from the dialogue-box the user given values and writes into a file, whereas, ' OnLoad Param ( )' routine read from the selected '.par' file and reset the dialogue-box control with these values.

4.3.1.4. 'Save ndata as' Interface (Fig. 4.11a)

The 'ndata' array stores the degraded chain distribution data, generated by a simulation experiment for each time cycle, it can be saved to a file by selecting and clicking 'Save ndata as' submenu of the 'File' menu in the main frame-window interface as described earlier. This would prompt the 'OnFileSavendataAs ( )' function to save the data from the array together with their respective time data. The former is saved into '.ars' files separate for each time-cycle and a list of the 'ars' files together with the time data is saved into an '.idx' file. These can be accessed from the 'Exppar' interface to read back into the program for redisplay at a later time. The loading is displayed as shown in Fig. 4.11a. This way of keeping a record of simulated distribution data saves rerunning experiments and/ or saving a large number of large '.BMP' files of the saved images. Image saving techniques and formats utilities are discussed in section 4.6.

4.3.1.5. 'Save Bitmap as' Module

The bitmap is an array of bits containing data that describes the colours found in a rectangular region on the screen. The number of bits of data in a colour plane represents a single pixel. Upon pressing this button from the submenu, it activates the 'OnFileSaveAsBitmap( )' function, which calls for two subroutines – (1) 'CreateBitmapInfoStruct ( )' that initialise a 'GDI' graphic 'Cbitmap' object with the selected bitmap image colour pixel data, (2) 'CreateBMPFile ( )' that creates a '.bmp' file format to convert and store the image. Conversion can be done by other ways very quickly such as via control print screen keys on the computer keyboard. The image from one window application can be dumped into another by pressing a combination of three keys such as 'shift', 'alt' and 'SysRq'
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**Other Important Interfaces**

Figures 4.11a-c: (a) pre-saved data-file interface to select `.idx` file containing a list of `.ars` data files in the order of time (hours), (b)`Exppar` interface List box reads the `.ars` files from the above sequentially by the class `CExppar` member functions and package these variables into `CPolydegView` class to display at the output in the form of MWD, (c) Data Rendering dialogue box - provides hiding or smoothing options for MWD curves for one or a number of time cycles.
4.3.1.6. Experimental Data Interface (Fig. 4.11b)

Top left-hand side (LHS) edit boxes are used for graphic co-ordinate scaling purposes. Top right hand side (RHS) radio buttons are incorporated mainly to set the mode of graphic and result display. Middle control boxes are associated with the reading of external files, printing filenames or file pathnames etc, in order in a 'Listbox'. Bottom buttons are there to perform final editing of the 'Listbox' in various ways.

'Delete one', 'Delete all': deletes only selected filenames one by one or all.
'Previous dataset': re-enters the previous filename list that was used for the previous run, for re-use in the next model run.
'Scroll bar': on the RHS of 'Listbox' serves scroll a selected file pathnames up and down on the list to re-order as desired. Before any kind of editing or manipulating by the scroll bar, a file pathname has to be selected. Any selection is highlighted as shown above.

Ok and Cancel buttons: when Ok is pressed the Expper class module begins processing the user commands given in the interface. The program reads in the selected files containing data and starts processing them to package data into 'View Class' ready for a model run. If the Cancel button is pressed the window disappears.

'Read data' controlbox: when pressed brings in a new window with datafiles saved as either "*.idx" or "*.ars" files. This lets the user choose an experimental data set with or without laboratory-recorded real times for inserting into the 'Path Listbox'. The latter is filled by the pathnames of the files below as displayed above for the read module. The control buttons at the bottom are all designed for ordering the file lists.

Path: presents a listbox to contain and display the filenames or file pathnames, in order of selection from the directory where the experimental data are stored. It displays a set of "*.ars" files with their respective lab-experimental time in hours, which are inserted into a list datatype for reading the contents of each in succession by the 'readfile' routines of 'Expper' class. The names of these files and the times are listed in a separate "*.idx" file, which, upon double click, will print its contents in the above listbox.
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control. This reading from a file mechanism is coded to eliminate one by one file pathname selection of '*.ars' files, which needs to be manually ordered.

'Choose Expdata as' radio buttons: provides a set of radio buttons to choose a desired graphic display for various comparative studies. It controls how the data files are used to feed values for an initial distribution for a simulation run. Alternatively, several / selected files can be used to provide superimposed graphs of simulated curves with lab-experimental ones.

Choose Time Display: mainly informs the program what sort of time distribution would be used from a menu list. Model details regarding the programming designs and functionality are given in section 4.4.2.

4.3.1.7. 'Data Rendering' Interface (Fig. 4.11c)

The above interface is created and appears on the main window template by the call of the respective functions attached to either of the 'Simulated' or 'Experimental' submenu of 'View' in the Main frame window menu, as described earlier in the main 'Menu Interface' section. The main purpose it serves is to abstract data from the graphic routine used for plotting, so that one/some of the selected distribution curves can be hidden from the display output. This eliminates crowding of set of overlapping curves in the view window and helps close examination of the contour of the curve / curves of importance. The subroutines attached to this interface can also prevent data from being sent for smoothing by the smoothing routine. The latter operation may sometimes blur the subtle deformities around the peak areas and make them unnoticeable. This may indicate an onset of an important chemical change in the curve such as a peak splitting in two or more peaks, the appearance of a shoulder near the main peak etc. These delicate changes in the curves, whilst being preserved, can accurately translate the extent of deflection from the initial normal or near normal form.

The RHS bottom two sets of tick boxes in Fig. 4.11c, are for curve 'Hide' and curve 'Smoothing'. The 'cycles' attribute printed beside the tick boxes is to mark the number of outer time cycles in succession. Those un-ticked boxes
are dealt differently from the ticked ones e.g. indicating not chosen for the respective abstraction. In this way the user can have options to include or exclude 'X' number of curves, generated from the model-run, for closer examination. This is a way of 'Zooming' operation and eliminates undesired obscurity or overlapping in simulated MWD curves. The data rendering mechanism is of vital use for viewing two sets of superimposed curves, e.g. when lab-experimental data curve-set are compared to simulated ones.

4.4. Implementation Strategies

Modern windows programming styles are interface oriented. Interfaces are the central driving forces to fulfil the objectives of a computer simulation program such as the current project. A number of implementation strategies can be schemed in order to make the program meet end-user demands while carrying out multiple tasks. A good design brings flexibility and reliability in a program, where many options can be opened to the user to run the program with ease and confidence. The previous section described in details the various uses and operations of some of the operational interfaces, and how they are linked with their respective implementation 'Base Classes'. Other modules furnish other operation such as various graphical plots, data structures to store curve co-ordinates, strategies used for curve smoothing operations (also discussed in chapter 3), printing text results in chart form etc.

Also different kind of strategies are used to implement various algorithms for mathematical computation, Monte Carlo and Markov chain probability matrices, calculation or deduction of real time to mark degradation, degradation models etc. Most of these will be dealt with in the next chapter, but details of two important implementation strategies are discussed here.

4.4.1. Multi-directional Access to Interfaces

(Fig. 4.12)

How an interface can be accessed in more than one direction and also how
any of its functionality can be potentially re-used to serve different purposes are demonstrated in Fig. 4.12. This example shows how a graph rendering function module such as 'Class CdataRender', which is connected to the 'Data Rendering' user interface, can be accessed directly prior to the 'Model Run' stage or indirectly after this stage as illustrated in the Fig. 4.12 diagram. The direct approach is schemed to yield a reformed graphical end result as desired or dictated by the user. The indirect approach can also furnish this result but after a normal graph plot display is examined and following that if the user decides to approach the interface for a reformed display. The same figure also demonstrates that the 'ndata-array' can be loaded by data via two routes – either via the usual procedure using the 'Data Entry' dialogue box or via the 'Expper' (experimental data reading and loading interface) 'Model Run', or from a pre-saved file e.g. a '*.par' file. In the second case 'Expper' can be approached to exploit its external file reading facility to feed data into the 'ndata-array'. This diagram also illustrates how different 'Base Class' modules are independently linked with the distinct functionality of each 'Interface' in a typical object oriented fashion.
Figure 4.12: exhibits diagrammatically (I) how an interface can be approached from different angle to accomplish the desired tasks e.g. ‘Data-rendering’ Interface can be approached directly before the ‘Model-run’ stage or after in order to get the reformed graphic display or (II) reuse of Interface for separate purpose e.g. ‘Exppar’ Interface is used here for reading pre-saved ‘Model-run’ data files, whereas its other vital use is reading and extracting experimental data from external file source.
4.4.2. Experimental Interface Operation Flowchart
(Fig. 4.13)
In chapter 3 the disadvantages and visual obscurities involved in graphical plotting features of existing simple models, are discussed. The steps and strategies that were introduced to eliminate these difficulties are detailed. The enhanced simulation models and graph plot operations are now explored to make a comparative study with lab GPC experimental MWD data curves and their individual relative trend to shift from a HMW to a LMW region of the XMW-axis. This will now enable us to statistically determine their closeness of fit to a theoretical model. The programming and design aspects involved in the implementation of reading in and processing of experimental data with a suitable "Interface" is exemplified in this section.

The figure 4.13 outlines the scheme designed for the basic data flow and operational architecture that would account for different frameworks of experimental data uses to achieve different perspectives. Firstly, the required data set needs to be extracted from GPC raw MWS data files. These are then stored in separate text files for future uses. The latter files become the source files, from which program reads the raw data into an Exppar Class module. This module is designed and incorporated specially for dealing with experimental data and is functionalised to deal with different data sources. Finally, the data are displayed graphically to an appropriately chosen scale through a graphic processing routines of the View Class.

4.4.2.1. Experimental data reading Interface Layout

The grouped radio buttons displays separate options pertaining to different data categories, two of which are displayed above. One deals with a different form of data display in the output. The other refers to respective time display, acquired from a different source. Only one item can be chosen from each group. Here - “Experiment data display” is chosen in the first group and “Simulated degradation” for time display. The “Read data” button, when pressed will display the file open interface, to display the files to be
Fig. 4.13

Select Submenu Item from Mainframe Window Interface + Click to send command to open Main Experimental data interface

Experimental Data Input Interface
Default Appearance

Click Previous-Data Import Command Button

Yes

No

Click Read-data Command Button

Yes

No

Select the Radio-button from the two categories

Yes

No

Open the "Open File" Interface

Select Files

Set New Values
Set Default

"*.am" 
"*.idx" files

Serial Selection
Set Selection

Enter File-Pathname List in ListBox Control Order List by Pressing Desired Command Buttons

Add One
Delete One
Change Position

Yes
No
Yes
No
Yes
No

Click OK Button
Click Cancel Button

No
Yes

Yes
No

Retrieve Data from Files in appropriate Data Structure Scale, Modify, Channel Data according to Display Selection

Flow Chart Of Exppar
read in the List box area tagged as "path. The command buttons at the bottom of the interface are there to provide extra flexibility, means and stability in making a choice of the data files to be imported.

The following accessory interface is used for the selection of required files and importing data from those files. These files are text files and are distinguished from the others by special file name extension as "*.ars" or "*.idx". The first is used for naming files containing data and the second signifies files containing the names of each set of data-files with corresponding lab-time index. The following interface exemplifies this.

In the above serialised interface is highlighted a filename with extension "*.idx". The content of the latter is shown in the main interface given in the last page. Further the above interface also shows a number of files with "*.ars" extension, which contain actual extracted GPC data of MWD of a particular type of cellulose material, which has been degraded by means of accelerated ageing.

4.4.2.2. Implementation Algorithm

Data Structure: Main data storage types used for storing file pathnames and extracted data are different classes of linked lists. The latter involves CListBox class and CList template classes.

The CListBox class provides the functionality of a Windows list box. When the user selects an item, it is highlighted and the list box sends a notification message to the parent window. CExppar class constructor creates the CListBox object, by calling an appropriate member function and declares a list-box member variable. On creation of the Windows list-box control, this is attached to the CListBox object. To use a list box in a dialog template, as in CExppar class dialogue interface, a DDX_Control is used in the class's DoDataExchange function to connect the member variable to the control. Though a member variable object's belonging to the ClistBox class inherits its functionality with regard to ordering, manipulation etc., it was necessary
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to implement some separate functions in order to perform some of these
tasks the algorithm demanded. For example CListBox class does not have a
suitable multicolumn facility. As mentioned earlier, two file types are
displayed and one ("*.idx") type required multicolumn display of file
pathnames and corresponding lab-based times. The second category of
linked lists implemented is of the type-safe template-based collection class
data-types in MFC version 3.0 and later. Using these templates to create
type-safe collections is more convenient and provides better type safety
than using the collection classes not based on templates.

The CList class supports ordered lists of non-unique objects accessible
sequentially or by value. CList lists behave like doubly linked lists. A variable
of type POSITION is a key for the list, can be used as an iterator to traverse
a list sequentially and as a bookmark to hold a place. A position is not the
same as an index, however. The main advantage of using linked list is
fastest element insertion at the list head or at the tail or at a known
POSITION, than any other data types i.e. array, map or graph.

4.4.2.3. Interface Module Operation (Fig. 4.14)

The following Fig. 4.14 illustrates how individual interface modules carry out
user given commands, manipulation and different processing of raw data
sets. These are cited in a series of flow chart like diagrams. User commands
take different routes through the network of C++ Class structure, using the
respective objects as required. This flow of modified data finally ends up in
the graphic display output module that is responsible for finally
synchronising parallel operation and in bringing up the desired effects.
After data are read and retrieved from storage files they are packaged into
suitable data structures in the Exppar class module, these are then passed
to the next appropriate modules for further treatment. During raw data
reading and retrieval, linked lists are used for storage, the latter are
substituted by an intermediate array to store the scaled and reform data.
Further treatment of data is required for different choices of graphical
display. Fig. 4.14 exhibits infrastructure of ‘Cexpper’ Class and its various linkage with other Classes and user interfaces.

4.4.2.4. Discussion of Code Structure

It is not possible to include all the functions of the “Exppar” module within the limited space and requirement. One of the main procedures “readexpdata” is briefly exemplified in Appendix 4.

4.5. Complex Network Interface - Slider Models

4.5.1. Slider Model I (Fig. 4.15 a-b)

A slider model provides the means of combining various chain scission models in order to widen the scope of a simulation experiments. Each slider arrowhead can be slid to a value presenting a pre-selected percentage signifying an individual rate of occurrence per selected model. The percentages carry probability weights, which are calculated from the total on an individual ranking basis thus controlling the occurrences of a scission process per each time inner-cycle orbit as dictated by their priority ranking. Fig. 4.15 a-b presents a layout of Slider I user-interface.

This strategy helps to achieve a blend of selected models for a particular simulation experiment. Thus for example if slider Fig. 4.15a arrowhead is set to 80 for model “Unzip”, its frequency of appearance will be 80% of the total degradation duration. Likewise, if “WeakLink” rate is selected 2%, its occurrence will be 2% of the total. Fig. 4.15a-b illustrates the mechanism of setting rank order (e.g. 3) to each selected scission model (e.g. Unzip) from the combination per each time-cycle (e.g. 3).

The bottom combo-boxes keeps the list of some of the simple models e.g. ‘Random Time’, ‘Cut&Chop’ etc. The model allows more varied or complex versions of the simple models. For example the model may allow, chain fragmentation to initiate at different times for polymer segments depending on their molecular weights. Thus steric hindrances can be imitated as the
Fig. 4.15a-b: display various features - horizontal slider (topmost) is set for a timecycle 3, vertical sliders (middle) are set to weighted percentage of occurrences of the selected scission events, bottom control boxes are used to set their ranking order of occurrences during a model-run, e.g. (a) shows event 'Unzip' is being selected from the model list and (b) its rank (3) order is being selected for timecycle 3 (displayed at the LHS control box), the 'model-run Mode' is selected 'Preferential'.
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location of the latter varies throughout the various sections or lattices of a polymer structure. The "Mode" radio-buttons enable selection of primary techniques that control and manipulate the nature of the reaction as well as the calculation process of polymer chain distribution during temporal degradation. The latter is dependent of the former to some extent and range from statistical iterative Monte Carlo methods to mathematical or instant calculation etc. Thus Slider I interface presents a powerful computer modelling strategy for a far more complicated chemical process such as polymer degradation.

4.5.2. Slider Model II

(Fig. 4.16 a-d & Fig. 4.17)

This presents another example of computer based simulation strategy that allows the incorporation of additional complexity into a model by defining "Degradation Zones". The user can manipulate its various control box machinery, in order to create degradation reaction zones. A layout of various features of this window style interface design is displayed in Fig. 4.16 a-d. How the user can access the interface is indicated in diagrammatic form in Fig 4.17. Fig. 4.17 also illustrates some details of Slider II implementation 'Class' and its member functions. Slider II control-boxes functions are described below.

'Specify Total Time' edit box (top LHS): take an integral value to specify total time for degradation reaction, total time is divided into several smaller time segments or units to distinguish different time events with regard to evolution of reaction parameters and so creates separate time zones.

'Set Polymer Type' combo-box (middle section of the top): this is a pull down combo-box, which could contain a list of polymer names. This is linked to a function called 'OnSelChangePolymerTypeCombo ( )' (see Fig. 4.17). The latter is programmed to test the polydispersity of an initial molecular weight distribution and its subset range to inform the program whether the polymer is composed of larger molecular weight chains or how widely varied are its
various weight fractions. Depending on this the function then alters the interface attribute value settings. When the user highlights a name, this function changes the layout of all the labels of the interface and sets them to those suitable for the selected polymer type. This action is demonstrated in Fig. 4.16 c and d, displaying different set labels of polymer type-range that changes automatically as the user changes the selection from the 'Set Polymer Type' combo-box list (highlighted). For this kind of automatic change mechanisms to take place in the control-boxes contained in the interface were implemented in its program module. There are functions, responsible for triggering each set-up change for displaying and modelling separate 'Degradation reaction zones' for the individual time-cycle (4.16 a-b) as well as for each polymer type (4.16 c-d).

'Set Degradation Zone' (Middle): This is the important section that enables the user to create a reaction cluster. This section is designed with a set of horizontal radio buttons labelled as 'Location 1', 'Location 2' etc., a set of horizontal sliders labelled as 'Deviation Band' and a set of vertical sliders labelled as 'Set Kinetic Rate 1', 'Set Kinetic Rate 2' etc. The former simulates preferential bond location (either end or middle) sites, where a scission is most likely to be performed, along the backbone of a selected chain from the total polymer population, depending on what subset group the chain belongs to. 'Deviation Band' sliders are set to mark the width of the standard deviation around a selected mean, referring to the chosen bond location site. These parameters determine a normalised non-uniform PDF in order to vary the scission bond location site per across a large number of iterations. The vertical 'Subset' sliders simulate varying kinetic rates for the individual DP subset domains. Each slider set is labelled with a DP subset range. This would enable the researcher to account for various factors that may affect a reaction rate, which is dependent on temperature, extent and type of crystallinity, structural segments containing more functional group density etc. This model thus allows for varied simulation mechanisms, widens the scope of simulation experimentation, caters for non-uniform, complex reaction kinetics etc.
Window Interface Design for Slider II Model

Figures 4.16a-b: show automatic changes in 'Degradation zone' section - vertical and horizontal sliders and radio-buttons for each change in time-cycle set-up by the horizontal time-slider (at the very top). These are to be previously set by the user for each simulation experiment-run - e.g. (a) shows a set up for time-cycle 3 and (b) the same for time-cycle 4. Thus the interface work as experimental protocol directing the computer program execution.
Figures 4.16c-d: show automatic changes in 'Degradation zone' section set-up per different selection of 'Set Polymer Type' combo-box (at the very top). e.g. (c) DP-range changes at the higher scale 1-20,000 for Polymer type 4 and (d) scale goes even higher 1-42,000 DP for Polymer type 5.
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'Specify Time Range' horizontal slider (top of middle section): This is a slider box drawn in a horizontal dimension style to represent the segmented time outer cycles. The total time is divided into 10 divisions referring to 10 time-segments, the duration of which may be different. This is to mimic unequal hourly real time when the state of polymer chain degradation was observed experimentally in an accelerated laboratory test. Each time-segment or cycle, is memorised from the horizontal time slider by means of the 'Process Time Slider Click ()' member function of 'Class CTSliderdlg' as shown in Fig. 4.17. The functions 'OnVScroll ()' and 'OnHScroll ()' are used to keep a record of all the respective positions of the 'Bond Location' radio-buttons and the vertical 'Subset' sliders set for each 'Time-cycle'. These are stored in the 'Class's member variables for further packaging of data. One of the advantages of this design is that once these various control box positions are set, the user can check them by sliding the Time slider arrowhead backwards along the horizontal line, as these positions will change automatically. So this eliminates the problem of remembering so many individual probability values for each cycle etc.. Also Time slider remembers these positions for subsequent model runs and hence the user does not have to reset these values repeatedly unless the user wants to alter any. These are demonstrated in Fig. 4.16 a-b.

PDF (Probability Weighting function) section (top left): enables the user to build either a discrete weighting PDF as a Rectangular PDF or a more continuous Probability Density distribution as a Triangular PDF. The functions are calculated from the 'Subset' slider weight-data by 'Class CSlider' member functions. The selection is recorded by 'OnPdfRectan ()' and 'OnPdfTrian ()' member functions of 'Class CTSliderdlg' (see Fig. 4.17). Preferential degradation can be graded by differential speed of participation in the polymer sub-population.

This model has been found most efficient of all and also convenient for lognormal scale experimentation, as will be shown for models of the GPC distribution curves of a Cellulose substrate in chapter 6. The ultimate aim would be to link slider II with slider I for the purpose of complex polymer
Figure 4.17: illustrates how Slider II user-interface can be accessed by the user via main ‘Data-entry’ dialogue box (at the top), the interface is linked to a ‘Class’ – ‘CTSliderDlg’, which is a ‘friend Class’ of ‘Class CSlider’ in inheriting some of its properties to add to extra functionality (middle part), it’s own member functions are displayed with function symbol ‘()’, at the bottom part of the figure, stating what action each member performs (in red labels), when their corresponding control box is mouse clicked or edited by the user.
systems or to simulate complex environments leading to a cluster of
cOMPeting reaction situations.

4.6. **Cubic Cspline Algorithm**

*(Fig. 4.18 a-c)*

To maintain the accurate curvature is not an easy task. It requires
application of a method of interpolation, frequently used in modern computer
graphics. There are various types of interpolation methods and algorithms.
Cubic Cspline algorithm has been used and implemented here. This has
been found to be easiest and most ideal in tackling the present problem.
The power and sophistication of this method is demonstrated in Chapter 3
where the initial problems in achieving desirable simulation of the GPC
derived MWD curves are discussed in details. The detail of mathematical
background and concept in deriving this smoothing algorithm is given in
Appendix 5.

Three options are offered in the Main window interface Menu Item
'Smoothing' – (1) None (i.e. no smoothing), (2) Average smoothing i.e. line-
smoothing or (3) Cubic Spline i.e. refined curve smoothing (Fig. 4.18a). The
selection would pass a command to the program to carry out this task
accordingly for processing the output graphs after a model-run. The third
option also provides an interface that contains an index of parameter 'Pval'
(Fig. 4.18b). The latter is a real number that controls the extent of smoothing
(Fig. 4.18c), accessible in the submenus 'Smoothing Params'. This can be
altered to higher or lower values depending on the degree of interpolation or
smoothness required.
Interfaces For Smoothing Operations

Fig. 4.18a: displays the ‘Smoothing’ interface, showing three options or submenus in the ‘Smoothing’ submenu – ‘Cubic Spline’ is the best curve smoothing technique and most efficient in dealing with large number of coordinate points in graph plotting.

Fig. 4.18b: ‘Pval’ interface controls the degree of smoothing.

Fig. 4.18c: Shows the effect of ‘Cspline’ smoothing (RHS) of unsmoothed curves on LHS.
4.6.1. Example of Class Inheritance
(Fig. 4.19)
The smoothing module was initially written in C language and then imported in MFC Visual C++ project, the software platform being used for present modelling. This module is then further improved and redesigned in the form of abstract and inherited class modules. The latter form of OOP is called "Inheritance". The modules are customized version and are exclusive of the MFC Visual C++ class library. The purpose of this modification was for better compatibility with the later program design and principally for faster and more efficient use of code and reuse of modules. An outline of this design concept is given in Fig. 4.19. This shows a hierarchical relationship between the base class "Psmooth" with the derived classes e.g. "C spline_Smooth", "C Average_Smooth" etc. as an example of inheritance.

4.7. Techniques for Image Manipulation

The simulation work in the current project involves a lot of graphical output in multicolour images. These images need to be stored in an optimised format, which efficiently preserves their colour pixel quality, positions and resolution for both curves and text. It is necessary to use a multiple colour palette for ease of marking separate time-curve and date sets and to prevent confusion. Editing and cropping operations are necessary to fit images to a particular size of paper. BMP and GIF file format are found the best for accurate preservation and storage of colour images, but the GIF format is more highly compressed and therefore saves disk space. 'Paint' and 'Paint Shop Pro' version 7 were used for image manipulation in Windows and 'GIMP' Gnu image editor software was used for UNIX. This was used in conjunction with a colour pixel co-ordinate-reading program for the purpose of converting colour pixel co-ordinates to normal screen co-ordinate data. This operation was required to extract lab-experimental data from scanned images of published MWD curve sets. The program was written in 'Perl', an object oriented programming language, in order to run in UNIX system. More information regarding the image formatting and
Example of Object Oriented Class Design

Abstract Class

PSmooth

Class CAverage Smooth

Graphic Output Interface 1
Plot MWD Curves Using Average-Smooth routine

Class Cspline Smooth

Graphic Output Interface 2
Plot MWD Curves Using Cubic-Spline Smooth routine

Class Cno Smooth

Graphic Output Interface 3
Plot MWD Curves Using none

Fig.4.19: Class Inheritance of ‘CSmooth’
4.7.1. Extraction of Experimental Data

12 sets of MWD curves for two cellulose cotton types were available as scanned images from accelerated ageing tests at three temperature and two kinds of medium (oil and air). These data form the basis of the modelling tests described in Chapter 6, but the original data were not available due to a disk fault, so a program was written to regenerate the data from the bit maps. Colour pixel co-ordinate data were obtained from the scanned images of each MWD curve set using a ‘Perl’ program under the UNIX operating system environment. This program is designed to identify each curve contour from overlapping curve sets by their distinct colour code, read the pixel co-ordinates and convert them into screen co-ordinates. The latter data were saved in ‘*.ars’ files for appropriate scaling. The maximum and minimum pixel co-ordinates for each set were detected and recorded in an ‘E-macs’ editor file. RGB colour codes for each curve from the set were mapped to their corresponding lab-time in hours in ‘*.map’ files. After the raw screen co-ordinate data obtained from pixel co-ordinate data set, the former were scaled to the desired rendered data. This would fit the raw data in the Lognormal scale as given by the original scanned MWD graphs.

Some preparatory work was needed to remove all the spurious dots etc. from the original scanned image BMP files and to convert any two identical colour curves into separate pure colours etc. Thus colour filtering and conversion of each pixel dots belonging to one distinct curve contour from the set of overlapping curves, posed a difficult challenge. This operation was successfully performed by Gnu Image Manipulation Protocol (GIMP) software, which was imported from the Internet public shareware domain. This is a well organised image editor and works under the UNIX operating system. In order to execute these images editing operation the BMP files were required to convert into PNG format, as this format keeps highly compressed and precise pixel dot sizes.
4.7.2. Image Format Conversion

4.7.2.1. Raster Image Formats

A raster format breaks an image into a grid of equally sized pieces, called pixels, and records colour information for each pixel. The number of colours the file contains is determined by the bits-per-pixel: the more information recorded for each pixel, the more shades and hues the file can contain.

Most raster formats support multiple bits-per-pixel levels, and therefore more than one level of colour. Most raster formats record colour information on a pixel-by-pixel basis, but some formats use colour planes. Each colour plane contains all the pixel information for a single colour. Colour planes are also called colour channels. Formats that use colour planes/channels are called planar formats.

The bits-per-pixel are determined by multiplying the bits-per-plane by the number of planes. If the resulting number is not a power of two (expressible as \(2^a\), where \(a\) is an integer), then the bits-per-pixel are "promoted" to the next highest power of two. For example, if there are two bits-per-plane and three planes, the bits-per-pixel are promoted to eight:

\[
2 \times 3 = 6, \text{ and } 2^2 < 6 < 2^3
\]

For example, GIF v. 87a Interlaced (Compuserve) supports 1-bit, 4-bit, 8-bit colour, BMP (RGB encoded (OS/2)) supports 1-bit, 4-bit, 8-bit colour, 24-bit colour pixel size, PNG (Interlaced Portable Network Graphics) supports 1-bit, 4-bit, 8-bit colour, 16-bit, 24-bit, and 32-bit colour pixel sizes etc.

4.7.3. Image Formats (used in this project)

PNG (Portable Network Graphics) Format: is a format used to transmit and store bitmapped images. It was created specifically for the Internet and other networks. It provides alpha transparency, high colour support, and slightly
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better compression than GIF. The current generation of Netscape Navigator and Internet Explorer may not completely support PNG and previous browsers do not support it at all. While it supports alpha channels and creator information, it does not support layers. Reducing palette size to contain only those colours present in the image does palette optimisation. The palette colours are also re-arranged so that any transparent colour comes first. These steps reduce the file size.

GIF Format: GIF (Graphics Interchange Format) is one of the two most popular image formats used on the Internet. It supports up to 8-bit colour depth images (256 colours) and it is optimised for high contrast images and blocks of colour.

TIF Format: TIF (Tagged Image File Format), is a widely used file format from Aldus Corporation. It provides several types of compression. The TIF format supports one alpha channel per image if you choose LZW, Packbits, or Uncompressed for the compression type.

Bitmap (BMP / D|V) Format: BMP (Bitmap) is the native image format for the Windows series and OS/2 operating systems. It provides Run Length Encoding (RLE), though some instances that require the use of bitmaps do not allow the RLE versions. It does not support transparency or layers.

4.7.4. Types of Resolution

Working with computer graphics, one needs to be aware of the resolution of the image, the monitor, and the printer.

Image Resolution: An image is composed of small squares known as pixels. An image with smaller pixels means it contains more of them, and it therefore has a higher resolution, displays more detail, and is a larger file size than an image with bigger pixels. Image resolution is the number of pixels per unit of length of an image, and it is usually measured in pixels per inch (ppi).

Monitor Resolution: Monitor resolution, which is the number of pixels per unit of length on a monitor, is usually measured in dots per inch (dpi). The resolution of PC monitors is approximately 96 dpi.
4.8. Conclusions

A software program was developed and enhanced to a standard to enable to carry out the simulation experimentation at satisfactory level. This helped to achieve the various objectives required for an independent simulation study for a deeper investigation into polymer degradation chemistry. This program supplied a complete tool to derive all the results presented in this thesis. Some of the major developments in this software program are listed below.

1. Implementation of 'Cexppar' class and interface - provides functionalities that deals with external file reading, data sorting and their appropriate processing in order to obtain a required result at the output window. For example it deals with a range of Lab-experimental data file reading together with their intermediate processing to utilise the information contained in the data. This module also reads simulated data from external files. Its Listbox can read and store data extracted from several such files, which can be replotted for review. Thus the module facilitates the creation of a database to store simulated MWD data and related profiles for a large number of degradation experimental conditions.

2. Graphic modification, addition and extension of many new features. These were required to eliminate obscurity and other drawbacks of the existing graphic output, for clarification, optimisation of graph plots and curve shapes and to enable simulation studies of more complex degradation models in much large scale capacity. Some of these features are given below (see chapter 3, 4 & 5):

   1. Implemented and extended new graph plotting functions such as a number of Average DP plot, Bond scission profiles, different time distribution vs. bond scission profiles, graphical profiles of other attributes related to simulated temporal MWDs including the latter. Implemented a range of initial distribution functions such as
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Skew, Normal, Gamma, Beta, Weibull - those were used for simulation study in this project apart from lab-experimental data.

II. Multiple window views with individual graphic/text facilities per individual model-run enabling clarification and comparison of various graph plots from the mainframe window menus.

III. Colour palette implementation to display MWD curves with separate colour hues for further clarification.

IV. Implemented a curve smoothing algorithm – ‘Cubic Cspline’ that refined the simulated MWD curve plotting, enhanced clarity of their features, removed the rough appearances of the un-smoothed curve-edges in the random iterative models. This is vital for examining the distribution graphs and their temporal changes.

3. Introduced a new Computer modelling strategy – Slider I and Slider II schemes (see Chapter 3 and 5) and implemented their individual window style interfaces that provided wider scope of combinations of scission events and time-cycles and provided the ability to create ‘Degradation Zones’ to simulate complex reactor.

4. Developed and implemented other important features of the program and their individual interfaces which play important roles in creating easily accessible user interfaces to facilitate simulation experimentation. Various phases of degradation reaction can be thus more closely imitated through various stages of progress of a simulation experiment run. This also facilitates the monitoring of each step of the resultant simulated MWD profile from a sample run. A few are listed below as examples:

   i. Parameter saving and loading facilities for future re-use
   ii. Parameter reminder list box interface that appears by double clicking at any place on the model graph display window
   iii. Progress-bar utility providing information of the progress of the model run
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iv. Modification of toolbars and status bar - providing information on the state of the program or the command in use etc.

v. Data rendering functions and interface – provides further flexibility in plotting the chosen number and type of graphs for closer examination and avoidance of undesirable data cluttering etc.

5. Implemented of interfaces that display a number of related charts and tables pertaining to each individual simulation experiment. The numerical information pertaining to the input attributes and parameters and their resultant values following the completion of an experiment are important in obtaining a clear complete picture in addition to their graphical presentation.

These charts are listed below:

i. Bond scission and turnover rate and percent related attributes’ values
ii. Time distribution related parameters
iii. Moment related parameters
iv. Bond scission kinetics related parameters
v. Scission event related attributes’ values
vi. Probability distribution related parameters
vii. MWD curve attributes related parameters

In addition to displaying the above charts, the data can be saved and stored in individual external files. This would allow the construction of a complete database of input data and results of simulation experimentation.

6. The implementation of three main mathematical algorithms (Chapter 5) for modelling polymer degradation MWD profile and related time distribution changes - i.e. Poisson, Exponential and Rectangular Hyperbolic distributions (Chapter 7) and related kinetic parametric conditions.
Chapter 5: Mathematical Models

Developing New Mathematical Models of Degradation

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5.1. Introduction

So far simple scission reaction models have been studied in terms of the Monte Carlo iterative static method governed by application of probability chains that helped to achieve desirable MWD temporal changes from the original zero-time distribution of the intact polymer. These outcomes have been examined in chapter 3. The static models are more suitable to simulate simple, homogenous degradation where polymer chains are predominantly under attack by a single kind of degrading agent. However, it is not possible to use a single scission mode to model complex reactive environments involving multiple decay processes in competition with each other. To epitomize the nature of such invasion a number of issues need to be taken into account (described in chapter 2, and 3) in terms of chemical phenomena. The task involved interpretation of the chemical events in mathematical and computing terms from solution of the equations, calculation of MWDs to deriving other pertinent results and their implementation in the computer program. The present chapter develops mathematical models using a range of statistical applications from classical Markovian statistics to a new concept of an exact algebraic solution to describe the complex deterioration phenomenon of degradation. The simulation experiment results pertaining to this chapter will be presented in chapter 6 with additional quantitative investigation of kinetic parameters for cellulose degradation in chapter 7.

A method of process optimisation for calculation of polymer MWD from a conventional Monte Carlo iterative method to a statistical instant method is introduced. The advantages of this novel approach will be addressed. In addition this chapter also describes an enhancement of iterative Monte Carlo application that is reinforced with the support of computer techniques (Slider I and Slider II) to allow for more refined and rigorous experimentation with more flexibility and ease. A few non-linear mathematical models were derived in this project to calculate real time distribution. These are mentioned here and their concepts are presented in Chapter 7. The full
Chapter 5: Mathematical Models

details of all the mathematical models and the derivation of their respective equations etc. are available in appendices 5 and 7, which are included in the enclosed CD. Please note that only the main equations in the developments are included due to space restrictions.

The efficiency of these methods will be compared in chapter 6 results, with specific reference to cellulose, for which a plethora of experimental data was available.

5.2. Review of Mathematical Modelling

5.2.1 Kinetic Diversity at Molecular Level

The degradation process of linear polymers had been assumed in the past as a fully random process in the light of theoretical treatment. Early mathematical (statistical) models developed by Kuhn (1930), Freudenberg et al. (1930), Ekamstam (1936), Sharples (1957), and later refined by Emsley & Stevens (1994) towards the development of classical linear kinetic equation assume a random chain scission reaction with a constant bond breakage rate. Successful applications of these linear models of zero or first order kinetic characteristics were verified for linear polymers such as cellulose, chitin, polyolifins, where decay is subject to the influence of unique accelerator under simple experimental environments. But if the latter is replaced with the presence of multiple degrading agents as in the electrical transformer, the reaction processes would obviously becomes more complicated. It would be difficult to interpret the reaction trajectory in terms of various modes of change. The recent work of Emsley and Heywood (2000) examined this issue in more depth and came up with a unique solution. Their new rate equation exhibited the clear deflection from steady linearity in the resultant kinetics. The deflection becomes pronounced as the rate of bond scission shifts from steady uniformity to a non-uniform mode and becomes a non-linear function of time. GPC of the accelerated test samples shows a parallel apparent deviation from initial Gaussian form of
molecular distribution in the subsequent MWD partial decay curves. This will be tested in the simulation results at the molecular level.

Emsley and Heywood (2000) derived a non-linear relationship between inverse of DP and time with time controlled by a second rate constant $k_2$, to justify the sudden drift from initial linearity towards an exponential decrement (Emsley et al., 2000b). The variability in overall reaction speed indicates the existence of differential reactivity amongst the constituent chain subsets owing to their variable molecular sizes and most importantly structural rigidity. It will be shown in the present thesis that the former depends directly on the latter and as such is preferentially controlled by the latter. The influence of the temperature on this effect will also be examined. A number of other recent researches (Hill et al., 1992, Cosgrove et al., 1985, Viebke et al., 1994) also concluded the possibility of multiple type reactions leading to a non-random or preferential bond scission during the initial and intermediate period of degradation. Apart from kinetic modelling there is an obvious need for mathematical modelling of the simulated decay at the molecular level of the complex molecular dynamics in order to understand parallel changes in the molecular weight distribution patterns of the decaying polymer. This important information can only be discerned from examining polymer molecular chain fragmentation processes more closely.

### 5.2.2. Simple Statistics to Combinatory Analysis

Early investigation in this issue used mathematical calculations that lead to complicated painstaking derivation of equations using simple statistics (Kuhn, 1930; Mark and Simha, 1940; Montroll, 1940; Tucket, 1945; Tobolosky, 1957). In order to keep the equations less complex these mathematicians had to assume a monodisperse polymer system and the polymer chain dimension to be infinite. These statistical treatments mostly focussed on deriving averaging parameters such as moments and DP and only considered polymer chain size variation as side effect of the cleavage reaction and PCLD is thus under-estimated. However in practical decay
situations, most polymers are polydisperse where parent chains of each dimension are constantly cleaved and chopped into different smaller sizes during the decay process. This increases polydispersity. As a result, the new generation of product chains keeps expanding with gradual decline in the parent generation. Nanda and Pathria (1959a, b, c) investigated the process of fragmentation in a more innovative way, using combinatory mathematics and number theory to deduce the ultimate probable number and sizes of chain dissociation products in different reaction situations. Nanda and Pathria (1980) not only dealt with the transformation of a starting monodisperse system in becoming polydisperse in the course of polymer chain decay progress, they also dealt with a starting narrow polydisperse system undergoing broadening, which have not been dealt before. However, most mathematical and statistical treatments of chain dissociation phenomena remained hypothetical due to the unavoidable complexity of the equations and unavailability of modern advanced computers at that time.

5.2.3. Statistical Concepts for Monodisperse System

The central problem in characterising degradation phenomenon of linear polymers is to calculate the size distribution of the fragments after a given time. In order to make it easy and readily amenable to a statistical treatment, the process is assumed as a perfectly random one. Thus all the links between monomer units in a polymer chain population are assumed of equal strength irrespective of their different parent chain sizes and the given polydispersity factor was completely ignored. Likewise all the chains in a polymer system are regarded as equally accessible to reaction i.e. structurally and kinetically equivalent regardless of their mechanical and structural differences. The latter ignores effects due to individual chain dimension, regional location (specially in complex structured biopolymers), crystallinity, configurational integrity etc.. A German mathematician Kuhn (1930) was the pioneer in this area, who developed the theory of degrading an infinitely long chain and applied very simple probability considerations. Flory (1936) compared his statistical concept to degradation with the
Chapter 5: Mathematical Models

experimental results of polycondensation. The initial sharp distribution curve of the starting homogenous materials at high molecular weight gives an equally sharp curve of low molecular weight at the end of the degradation process. These hypothetical estimations did not deal with the intermediate stages of reaction. Later Mark and Simha in 1940 added some refinement of this treatment by considering the case of finite chain lengths. Thereafter, mathematicians Montroll and Simha (1940, 1941) improved the mathematics further using statistical mechanics. They started with a simple initial distribution function of normal or lognormal type, derived hypothetical polymer chain distribution of the effect of degradation, using first and second moments of size distribution. However the function equations and mathematical terms began to get lot more complex while attempting to calculate probable size distribution of the newly generated fragments at different stages of depolymerisation. This required use of Hermit polynomials and calculation of higher moments and computing part-by-part integration of separate size summation.

5.2.4. Statistical Concepts for Polydisperse System

It was Tuckett (1945) who attempted to extend the existing general theory to cover polydisperse systems. He used the Darwin-Fowler method and evaluated the function coefficients integrals applying method of steepest descents to derive intermediate size distributions. Yet his hypothetical number generating function (a polynomial) was only useful at high extent of degradation and only for a system of minimum degree of polydispersity. A close similarity was pointed out to finding partition energy among a set of harmonic oscillators (Tuckett, 1945) or finding the number of permuted partitions in theory of numbers, referred to as “compositions by Macmahon (1915) in combinatory analysis” (Nanda and Pathria, 1959a). Theoretical estimation of polymer chain probable size distribution could now be solved in terms of suitably formulated polynomials. The analogous polynomial coefficients can represent how many possible ways to make R cuts over N chains of length P to obtain a range of chain size distribution values from
0, 1, 2, ..., \( p (p=P-1) \) where \( p \) referred to the number of links in each chain. The former is worked out in terms of a new technique called “compound generating function” (Pathria and Nanda, 1959b). Though their technique is elegantly interpreted, each summation corresponding to different sizes involved elaborate multiplication of permutation terms.

### 5.2.5. Direct / Deterministic Approaches to Modelling

(Fig. 5.1)

In recent times—a rational shift from historic classical statistical mechanics to other direct or indirect mathematical modelling techniques has emerged. As the commercial use of polymers is proliferating so the need for realistic evaluations of both polymerisation and depolymerisation processes are called for. For the reactor engineers there are need to define and understand the product polymer properties in sequential advancement of reaction. This depends on how clearly either PCLD (polymer chain length distribution) or PMWD (polymer molecular weight distribution) can be expressed in terms of either moment generating functions or sets of mass balance equations, governed by the set of kinetic rate equations characteristic of a particular process. The numerical analysis techniques (diagram displayed in Fig. 5.1) were enhanced with a view to introduce more direct approaches when time dependent gradual polymerisation was conceived as a classical Markov or Poisson process. The former can be broadly categorised as deterministic or statistical (Fig. 5.1). Either of the latter or in combination is commercially used depending on the complexity of the process to guide the engineer to a satisfactory interpretation and process analysis in the end (Fig. 5.1). In the field of polymerisation these interrelated avenues are popularly used by reactor engineers (Laurence et al., 1988), where solution to correctly assess the intermediate molecular states is indispensable. The concepts of direct or deterministic modelling both are sought for either independently or in a combined way. Reactions are expressed in terms of moment generating functions or sets of kinetic rate equations. At best they yield moments of distribution of average values from which distributions are inferred.
Importing Two Main Mathematical Modelling Techniques in Estimating Temporal Depolymerisation Behaviour

Polymerisation Reactor Engineering Technology

Polymers
(Synthetic / Bio-macromolecules)

Reaction Mechanisms

Polymerisation Depolymerisation

Mathematical Modelling Solution Techniques

Deterministic Approach Statistical Approach

Transform

Discrete Continuous

Semi-Continuous

Moment-rate-equation

Sequential-integration

Direct Approach Recursive Method

Markov Chain Theory

Transition-probability
Rate-functions

Algebraic-equations
Relating-parameters

Solution

Distribution MWD/PCLD

Moments

Fig. 5.1
5.3. Concepts of New Degradation Models

Previous models of degradation were based on a simple random iterative method (Emsley and Heywood, 1995). In the current project three different mathematical techniques have been identified to improve the modelling of degradation mechanisms and simulation of MWD which are further developed to achieve simulation of more complex systems:

1. Monte Carlo dynamic iterative method
2. Algebraic exact-statistical semi-iterative method
3. Direct instant method (using Markov transition probability matrices)

These methods will be compared using the coin tossing analogy algorithm shortly for a clear understanding of the disadvantages of the first method and how modelling could be greatly optimised using methods 2 and 3. The fundamental concept of transforming the Monte Carlo iterative calculation method to more direct or instant method can be easily demonstrated from an analogy of simple coin tossing statistics. The key concept is narrated below.

5.3.1. Coin Tossing Algorithm

The expected probability of heads and tails are known. Therefore one can predict the number of heads or tails that are likely to be achieved after a given number of tosses. If a coin is thrown a million times the overall result will be expected to produce 500,000 for each event on average. The trial output may vary each time, slightly more heads or tails. But this is not important at this stage (in future research it may be of interest to know how it deviates from an ideal model). Ideally what is hoped to be achieved, is to be able to write a function or formula which takes the parameters - the initial distribution, initial number of molecules of a particular range of lengths, the time and in turn computes instantly an output of a sequence of resultant number of molecules left at each length, after a given time interval of bond
scission. In the case of the coin tossing example, this is easy to determine. We can readily derive an instant formula for a million tosses:

\[ H = 0.5 \times t \quad T = 0.5 \times t \]

The goal of the current research is to apply this concept to the existing polymer degradation models. This simple principle is further detailed next in terms of the algorithm analogy.

### 5.3.1.1. Iterative Vs Non-iterative Statistics

**Method 1** *Random iterative method*

1. **step1** Obtain a computer generated random number between 0 and 1.
2. **step2** If this random number is > 0.5, let Head = Head + 1
   else Tail = Tail + 1
3. **step3** repeat for all the number of inner cycles + outer cycles
   (Result will vary)

**Method 2** *Statistical generated method*

1. **step1** Head = Head + 0.5
2. **step2** Tail = Tail + 0.5
3. **step3** repeat for all the number of inner cycles + outer cycles
   (Result always same)

**Method 3** *Direct instant method*

1. **step1** Head = 0.5 * t
   Tail = 0.5 * t
2. no need to repeat. (Result always same)

Clearly the direct instant method is the preferred solution. So far current research indicates (but not conclusively) method 3 is possible to achieve for polymer degradation, while method 2 is already achieved. The latter is shown to be a very effective method and readily eliminates the disadvantages of method 1. A proven general theorem in mathematical notation is included in this chapter and those of the specific simple scission models are included in the appendix 5.
Different calculation routes (Fig. 5.2) were composed and tested over progressively longer degradation time intervals to find their potential for the transformation from iterative to instant generation of MWD decayed curves.

**Current Model Scheme**

*Simulation Techniques For MWD Temporal Behaviour*

- **Algorithms for MWD Calculation**
  - (in terms of total bonds/molecules)
  - Scission Procedures:
    - Random, Systematic, Non-Random

- **Monte Carlo Stochastic**
  - Design + Random Number Generator + Markov Chain Probability

- **Computer Slider**
  - Interfaces + Discrete Weighting Probability Rating & Ranking

- **Pure Maths + Expectation Statistics + Continuous PDF**

- **Iterative Only**
  - Molecular Selection followed by Bond Selection Per Unit Time-Cycle

- **Iterative Process**
  - Molecular Selection followed by Bond Selection Per Unit Time-Cycle

- **Semi-Iterative**
  - Molecular Ranges & Bond Location Selection on Time Range Scission

- **Non-Iterative**
  - Formula Computed Expected Values of Molecular Species - Short Time Range
    - Instantly Computes Expectation Values of MWD Changes for Longer Duration

**Fig. 5.2: Scheme for introducing new mathematical modelling approaches for easier and faster evaluation of the outcome of polymer chain fragmentation processes.**

Note: This scheme was done before any development. A new addition to this was Markov chain (MC dynamic method) model that can generate instant calculation of MWDs on an hourly basis simulating the outcome of a complex reaction strategy as an alternative to the computer Slider model.

5.3.1.2. **Problems Associated with MC Methods**

The problems associated with the simple random iterative models of Emsley and Heywood, in achieving a desired MWD simulation have been discussed in chapter 3. These resulted in intensely uneven, jagged edged, obscure curve contours with an absence of sideways curve shifts and other important
Inadequacy in achieving a controlled outcome as inherent in the MC iterative approach called for more innovative and faster process design incorporating new mathematical concepts. New algorithms for MWD calculation methods were developed applying the principle of Markov statistics and an algebraic exact probability formulation to measure the outcomes of the time dependent chain scission events. These two mathematical strategies not only reduced or eliminated the large repetitive nature of iteration and other drawbacks but also enhanced the implementation of more complex degradation strategies. The iterative algorithm is flexible but poor in reproducibility. The new instant methods comprised more formative mathematical terms with more reproducible and faster outcome.

Simulation modelling in the polymer degradation area is very new and has usually involved Monte Carlo iterative approach (Rapoport and Efros, 1995; Radiotis and Brown, 1997; Huang et al., 1995). MC method may be more popular in the case of polymerisation (Yang and his groups 1988a, 1988b, 1990) but direct application of Markov transition probability matrix for the calculation of polymer chain length distribution has been shown possible by Lowry (1970). Only simple Markov statistics were afforded by Huang and his co-researchers (1995) to determine an average MWD from degraded...
samples. The application of such advanced stochastic probabilistic models has thus yet to make a major impact in the field of depolymerisation for easier and more productive outcomes than MC iterative or analytical methods (Suwanda et al., 1988; Tzoganakis, 1988; Ryu, 1991; Triacca et al., 1993). This thesis shows alternative means of simulation through computer aided numerical solution.

In the next section an account of the application of a Monte Carlo stochastic dynamic model towards the development of a complex scission network using computer interfaces is given before moving into the development details of the direct / instant calculation approaches in the later sections.

5.4. Derivation of Mathematical Models
The three mathematical concepts discussed in the previous section, are described in this section in terms of deriving the model equations and algorithm design were tested in defining cellulose degradation.

5.4.1. Monte Carlo Stochastic Model
Monte Carlo (MC) methods can be applied to any experimental or model system with purely random characteristics. This implies a rationalistic translation of an indeterministic unclear situation into probabilistic terms and treating it directly as a probabilistic problem. Application of transition probability could be iterative as formulated in the Slider computer model or non-Iterative if the Markov matrix is used.

5.4.1.1. Transition Probabilities and State Identification
Transition probabilities are usually constructed on the basis of analytical lab-experimental results. In essence the important parameters such as kinetic rates, temperature, environmental conditions etc. can be simulated in numerical terms by means of the former. Repeated random selection of one such element from an array of transition probabilities can be used to
mimic an event is about to occur in a random event oriented system. The events constitute different state components of a dynamically changing system. This concept is used in designing the Slider model complex network. A general formulation of such application (Burns et al., 1981) may progress as follows:

I. Identification of the states $E_1, E_2, \ldots, E_n$ of a real system

II. Formulation and Computation of the transition probabilities $P_1, P_2, \ldots, P_n$ corresponding to these states in predicting their chances of success etc., e.g. the system may adopt a state $E_i$ the chances of which would be guided by the probability $P_i$.

III. Generation of random number $x \in (0,1)$. The state $E_k$ occurs if the following inequalities hold

$$\sum_{j=1}^{k} P_j < x < \sum_{j=1}^{k+1} P_j$$

This step is repeated as many times as required and the inequality may be stipulated by any type of restrictions as demanded within the framework of MC models.

5.4.1.2. Variance Reduction by Sampling

A statistical sampling procedure is applied to each set of calculated temporal MWD decay curves. Two methods of calculation have been developed - a triangular and a rectangular continuous PDF. Both methods have been utilised in creating degradation nucleation centres and their progressive proliferation in Slider I and II model interfaces (described in Chapter 4). The first method samples a random quantity from sequentially weighted polymer reactive zones imagined as an infinitely large system. The second method samples a random quantity from a finite range of selected reactive zones where extents of reaction proliferation solely depend on the respective
weights. The extent of invasive scission rate on the selected finite zones are thus governed by differences in probability endorsed at the experimental interface of Slider II for each time cycle. Distribution of the slider weights are formulated in such a way for both methods in order to make the sampling process adequately responsive in differentiating an infinitesimal change $\xi$ among the weighted point co-ordinates forming a gradual increasing or decreasing chain. Slider I dictate probability of the successes or failures in activating a scission event from a selection of weighted probable events where a ranking system operates restraining their order of occurrence that obeyed certain inequality such as $\xi < p$ being satisfied.

5.4.1.3. Slider Interface Technique

This technique uses the computer window interface vehicle in harnessing a MC dynamic model application in a more realistic and sophisticated way. Most of the situations occurring in reality, in an uncertain fashion can be simplified enormously in a computer simulation. Although precise simulation of the real experiment with all information is not even necessary, both Slider I and II techniques in combination can successfully capture diverse and competing reaction features of a polymer degradation process. The overall randomness of the process also has been preserved by means of a dynamic random walk through the progressive temporal state changes. The entire invasive process is considered as a chain of finite time segmental operations as Markov process. The basic mathematical problem solution can be compared to other random but yet specific processes, such as problems in neutron physics formulated in a probabilistic way (separation of signals from a random-noise background) (Shreider, 1966). The computer window dialogue interfaces of both Slider I and Slider II and how they operate are described in chapter 4 (sections 4.5.1. and 4.5.2.). The parametric orientated application of the Slider model enables one to explore simulation experimentation at more depth and flexibility. This helped in building a complex scission network to model complex reactor system. How changing various parameters (those can be set at the interfaces) can exhibit
parallel changes in the results are illustrated in chapter 6. The following two PDF methods are kernels to this model.

5.4.1.3.1. Triangular PDF (Fig. 5.3)

The name 'Triangular' is denoted to this method of creating a continuous chain of weighted probability densities by means of calculating areas enclosed in a set of inter-connected, adjacent triangles. The calculated values were required to address the unknown weights for those points located along the bases of the latter. The latter connect the weight-points, given by the users in the set of vertical Sliders, (see Chapter 4 section 4.5).

Calculation of the areas underneath each points along the base that is either in a gradually increasing or decreasing slope is deduced from the series of similar triangles at the base points, whose sides are known to be in constant ratio for each original triangle formed between two successive weight points. A general expression (A) presents the mathematical function used for this calculation. Fig. 5.3 illustrates the mechanism.

\[
\omega(n,t) = \int_{S_i}^{S_j} \frac{d(n,t) \psi(n,s_i) \lambda_1}{T(t) \lambda_2}, \quad 2 \leq n \leq N, \lambda_1, \lambda_2 \Rightarrow \text{Weights}
\]

\[
\psi(n,s_i) = \int_{s_{i-1}}^{s_i} \gamma(S) \left( n \% \left( \frac{T(n)}{(T(S)-1)} \right) \right) ds, \quad 0 \leq \theta \leq \theta .......(A)
\]

Where \( \omega(n,t) \Rightarrow \) represents the weighted probability function of \( n \) (chain sizes and \( t \) (time). The RHS expression involves \( \psi(n,S_i) \) specifying a function of chain length and subset range parameters. The differential function includes subset range, bounded by lower and upper limits. \( \lambda_1 \) and \( \lambda_2 \) are constant coefficients for the fine adjustment of the slider weight continuous chain to work efficiently.
5.4.1.3.2. Rectangular PDF (Fig. 5.4)

The parameters of this PDF weight function values are derived from the diagonals of neighbouring parallelograms, each of which has one side common and are drawn at the middle point of the line joining two successive points on the X-axis whose probability densities are known (as selected by the user in Slider II interface). It is possible to deduce the unknown probability density values of each point located along the slope of any of such diagonals on the basis of the function expression (B). Fig. 5.4 illustrates the mechanism.

\[
\omega(n,t) = \frac{(Y_i - Y_i') \times (t - X_i') + Y_i' \times \lambda_1}{\lambda_2}, \quad 2 \leq n \leq N,
\]

\[
A_i = (X_i, Y_i), \quad B_i = (X_i', Y_i'), \quad Y_i = \frac{P(S_i)}{X_{b_i} - X_{a_i}}, \quad X_i = \frac{X_{a_i} + X_{b_i}}{2}, \quad S_{w_0} < i < S_{w_m}
\]

Where \(\omega(n,t) \Rightarrow\) represents the weighted probability function of \(n\) (chain sizes and \(t\) (time). The RHS expression involves \((X_i, Y_i)\) co-ordinates of the adjacent weight points located at \(A_i, B_i, \ldots\) in the Slider II interface, where \(i\) refer to the number divisions of polymer molecular chain subsets. \(X_i\) specifies the chain size intervals and \(Y_i\) the upper limit of the allocated weight in that interval. \(P(S_i)\) represents the comparative proportion of maximum probability weight per each molecular subset interval. \(\lambda_1\) and \(\lambda_2\) are constant coefficients for the fine adjustment of the slider weight chain to work efficiently.

5.4.2. Direct or Instant Calculation Methods

The starting point for new models was a very simple uniform distribution using fundamental expectation probability principle and algebra set theory. Application of the latter was then extended to Gaussian or Gamma
**Schematic diagrams of Fig. 5.3 Triangular and Fig. 5.4 Rectangular PDF calculation mechanisms.**

**Fig. 5.3**

Diagrammatic Presentation of How to Derive Continuous Triangular PDF for Slider II Dynamic Model

![Diagram showing the derivation of a triangular PDF for a slider II dynamic model.]

- Subset range $S_1$
- Subset range $S_2$
- Subset range $S_3$
- Subset range $S_4$

Area $a$ represents smallest to largest (i.e., $S_i$) proportion of the entire right-angled triangle $S_i$.

$(S_i, W_i)$ represents slider II interface allocated probability rate weights $W_i$ for each molecular size subset population $S_i$.

**Fig. 5.4**

Diagrammatic Presentation of How to Derive Continuous Rectangular PDF for Slider II Weighted Probability Model for Molecular Chain Subsets

![Diagram showing the derivation of a rectangular PDF for a slider II weighted probability model.]

- Interval $X_1$
- Interval $X_2$
- Interval $X_3$

$P(X) = Y = Y_1 + (Y_2 - Y_1) / (X_2 - X_1) \times (X - X_1)$

$P(X)$ = Probability density at an interval $X$

$(X_1, Y_1), (X_2, Y_2), (X_3, Y_3)$ etc. are discrete points where probability weights are allocated via slider II interface.

$(X, Y) \Rightarrow$ any point along the diagonals of sets of parallelograms.

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distributions and using the initial distribution of cellulose substrate used for accelerated lab-test. Application of this method was then further modified to incorporate different simple systemic scission models from purely random ones. Discrete forms were transformed into semi-continuous in order to achieve the ultimate goal of advancing the calculation of MWD directly or instantly. This eventually resulted in hypothesising the fact that despite the molecules breaking at random points at random intervals - scission is not a random phenomenon, from a statistical point of view (the coin-tossing analogy in section 5.3.1.). MWD calculations were enhanced with better results using the following methods than iterative MC method (described in chapter 3).

- Algebraic exact statistic method
- Markov probability matrix method

A theoretical model description of both the methods are given in the Appendix 5 and their application to polymers degradation is described in the remainder of this chapter.

5.4.2.1. Algebraic Exact Statistics Method

Primary Concept

See Appendix 5 for the full introductory details. A very brief account of the initial development of the formulae is narrated below.

The following proves total probability = 1 for N number of polydisperse chain lengths, where probability of a bond cleavage per each type of chain is weighted according to its frequency.

\[
\sum_{k=1}^{K} P_{k,n} = \frac{1}{\bar{T}_n} \sum_{k=1}^{K} X_{k,n} = \frac{\bar{T}_n}{\bar{T}_n} = 1
\]

So for each type of chain size k the probability was calculated as follows.
$X_{k+1} = X_k + 2 \cdot P_{2k,n} \cdot X_{2k,n} + X_{2k+1,n} + P_{2k-1,n} \cdot X_{2k-1,n}$ (for $k=1$)

$X_{k+1} = X_k - P_{k,n} \cdot X_{k,n} + 2 \cdot P_{2k,n} \cdot X_{2k,n} + X_{2k+1,n} + P_{2k-1,n} \cdot X_{2k-1,n}$ (for $k=2, \ldots, N$)

$P_{k,n} = 0$ (for $k > N$)

$X_k = X_k - \frac{(X_{2k,n})^2}{T_n} + 2 \cdot \frac{(X_{2k+1,n})^2}{T_n} + \frac{(X_{2k-1,n})^2}{T_n}$

$= X_k + \frac{1}{T_s} \left[ 2 \cdot (X_{2k+1,n})^2 + (X_{2k,n})^2 + (X_{2k-1,n})^2 - (X_k)^2 \right]$

### 5.4.2.1.1. Delta Correction

The above has been investigated and a corrected equation given below:

$X_{k+1} = X_k - P_{k,n} \cdot \delta + 2 \cdot P_{2k,n} \cdot \delta + P_{2k+1,n} \cdot \delta + P_{2k-1,n} \cdot \delta$

$= X_k + \frac{1}{T_s} \left[ 2 \cdot (X_{2k+1,n}) \cdot \delta + (X_{2k,n}) \cdot \delta + (X_{2k-1,n}) \cdot \delta - (X_k) \right]$

Where $\delta$ is the rate that determines to what extent reaction precedes i.e. the number of bonds broken per each time cycle. At the beginning, for simple models, $\delta=1$ was used, which assumed one bond-break on average. Although this produced accurate results, it suffered from drawbacks:

(i) Long run time of simulation program.

(ii) The equation is not flexible for experimenting with variable rates or incorporation of discrete rates for different subpopulations.

(iii) This is ideal for a model with rigid set rules – but cannot be expanded for complex degradation models.

Hence further research investigated for a more efficient and flexible approach that would primarily combat the slow speed.
Section 5.4.2.1.2. Modified Discrete Model – A General Theory

It was assumed that precisely one bond is broken at each step. This implies that only polymers of length 2 or more are picked at each step since monomers do not have any bonds that can be broken. Let $d(n,t)$ = number of molecules of length $n$ at time $t$. Then the total number of molecules at time $t$ is given by

$$T(t) = \sum_{n=1}^{N} d(n,t)$$

Where $N$ is the length of the longest molecule.

The following probability was structured on the assumption that molecules with the largest frequency would be most likely to degrade. The probability of rate of reactivity of a molecule of length $n$ at time $t$ is (ignoring monomers).

$$P(n,t) = \frac{d(n,t)}{T(t) - d(1,t)}, \quad 2 \leq n \leq N,$$

Where total probability must be 1 for each time cycle ($t$).

$$\sum_{n=2}^{N} P(n,t) = 1 \quad \text{(1)}$$

It is assumed that all molecules belonging to size group $n$ will have equal probability and once a molecule is selected for reaction all the bonds of this molecule are equally likely to react in the general case. But preferential probability is formulated for the other scission models (see Appendix 5).

In order to derive a formula for $d(n,t+1)$, it is assumed that each degradation event involves one molecule and one bond in this molecule is broken. What
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Effect this has on the number of molecules of length n is considered below. There are four separate cases to consider:

1. If a molecule of length \( k < n \) is chosen, then there will be no change in the number of molecules of length n.

2. If a molecule of length \( k = n \) is chosen, then the number of molecules of length n will decrease by one since a bond in this molecule will be broken.

3. If a molecule of length \( k = 2n \) is chosen, then there are \( 2n - 1 \) bonds, which are equally likely to be broken. If the middle bond is broken, with probability \( \frac{1}{2n-1} \), then the number of molecules of length n will increase by 2.

4. If a molecule of length \( k > n, k \neq n \) is chosen, then there are \( k - 1 \) bonds which are equally likely to be broken. There are two of these bonds, which could be broken to give a molecule of length n. Hence the number of length n will increase by 1 with probability \( \frac{2}{k-1} \).

The above four cases can be combined into a single equation as follows for \( 3 \leq n \leq N-1 \),

\[
\begin{align*}
\frac{d(n,t+1)}{d(n,t)} &= \sum_{k=2}^{n-1} P(k,t) \frac{d(n,t)}{d(n,t)+1} + P(n,t) \frac{d(n,t)-1}{d(n,t)} \\
&+ P(2n,t) \left[ \frac{1}{2n-1} \left( \frac{d(n,t)+2}{2n-1} + \frac{2n-2}{2n-1} \right) \right] \\
&+ \sum_{k=n+1, k \neq 2n}^{N} P(k,t) \left[ \frac{2}{k-1} \left( \frac{d(n,t)+1}{k-1} + \frac{k-3}{k-1} \right) \right] \quad \text{.................(2)}
\end{align*}
\]
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This can be simplified using (1) to give

\[
d(n,t+1) = d(n,t) - P(n,t) + \sum_{k=n+1}^{N} \frac{2P(k,t)}{k-1}
\] ...........................(3)

When \( n = 2 \) a similar formula to (2) applies but the first term is omitted since there are no molecules of length less than 2 which can be chosen. However, on simplification, the same formula as (3) is obtained with \( n = 2 \).

When \( n = N \), then there are no longer molecules and so it is not possible for the number of molecules to increase. Thus the last two terms of (2) are missing and the equation can be simplified to give

\[
d(n,t+1) = d(n,t) - P(n,t)
\]

Finally when \( n = 1 \), there are no bonds that can be broken but the number of monomers can increase due to larger molecules breaking. If a polymer of \( k > 2 \) length breaks, then there are 2 out of possible \( k-1 \) bonds that can be broken to give a monomer. For a polymer of length 2, there is only one bond and so that must be the one that is broken and there are 2 monomers formed as a result. Thus the required formula is

\[
d(1,t+1) = P(2,t) \left[ d(1,t) + 2 \right] + \sum_{k=3}^{N} \frac{2P(k,t)}{k-1} \left( \frac{2}{k-1}d(1,t)+1 + \frac{k-3}{k-1} \right)
\]

This can be simplified using (3)

\[
d(1,t+1) = d(1,t) + \sum_{k=2}^{N} \frac{2P(k,t)}{k-1}
\]

Thus to summarise, the equations for the degradation model are given by

\[
d(1,t+1) = d(1,t) + \sum_{k=2}^{N} \frac{2P(k,t)}{k-1}, \quad n = 2
\]

\[
d(n,t+1) = d(n,t) - P(n,t) + \sum_{k=n+1}^{N} \frac{2P(k,t)}{k-1}, \quad 2 \leq n \leq N-1
\]

\[
d(n,t+1) = d(n,t) - P(n,t), \quad n = N
\]
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The following proves that this model breaks only one bond at each time step by considering \( T(t+1) \) as required.

\[
T(t+1) = \sum_{n=1}^{N} d(n,t+1)
\]

\[
= \sum_{n=1}^{N} d(n,t) - \sum_{n=2}^{N} P(n,t) + \sum_{n=1}^{N-1} \sum_{k=n+1}^{N} \frac{2P(k,t)}{k-1}
\]

\[
= \sum_{k=2}^{N} \sum_{n=1}^{k-1} \frac{2P(k,t)}{k-1}
\]

\[
= T(t) - 1 + \sum_{k=2}^{N} 2P(k,t)
\]

\[
= T(t) - 1 + 2
\]

\[
= T(t) + 1
\]

The above is a general theory of the model for a random scission process. This can be modified to derive other specific scission model derivatives such as 'Cut in half', 'Cut Fixed Percent', 'Cut fixed Length' and 'Unzip'. The theorem and proof for each is included in the Appendix 5 (section 5.4.2.1.2). The following assumptions are made for these specific models:

1. Preferences are given to breakage of bonds at particular positions along the chain-length depending on the nature of scission mode.
2. Overall polymer distribution is polydisperse.
3. At each single time unit only one bond is broken.
4. The distribution is discrete and is non-stationary i.e. distribution varies with time as the bond cleavage continues.

5.4.2.1.3. A Semi Continuous Model

Since the distribution is not stationary as in coin tossing, the model derived here is equivalent to method 2 of the coin-tossing algorithm. In order to derive method 3 \( n \) and \( t \) must be treated as continuous variables rather than discrete. A differential equation of this model can then be formulated. This would be suitable for large numbers of long molecules. However the discrete
model can be transformed into semi-iterative if the probabilities attached to each type of chain breaking are considered stationary for small time segments (i.e. inner time cycles), which comprise the total time. This way computer run time can be reduced. Thus in order to formulate a semi-continuous transformation of this MWD calculation process, the Delta correction formula (see section 5.4.1.1.2.) can be utilised. The following equation refers to an example of MWD calculation of a chain-length \( k(2 < n < N) \) for the time period between \((t, t+\delta)\) in the case of ‘Cut in half’ scission mode.

\[
X_{n,\delta} = X_{n,\varepsilon} + 2 \cdot P_{2n,\varepsilon} \delta + P_{2n+1,\varepsilon} \delta + P_{2n+1,\varepsilon} \delta \text{ , where } 1 < \delta < \varepsilon , \ 2 < n < N
\]

This can be implemented in the general equation,

\[
d(k,t+\delta) = d(k,t) + \delta \left( -P(k,t) + \sum_{k=n+1}^{N} \frac{2P(k,t)}{k-1} \right) , \ 1 < \delta < \varepsilon , \ 2 < n < N \ \ldots \ldots \ldots (4)
\]

\( \varepsilon \) refers to a finite upper boundary. However simulation experiments showed that increasing the length of these stationary time segments (\( \delta \)) degraded the integrity of the MWD curvature to some extent. The smaller the magnitude of \( \delta \) the less is the significance of the latter. Some examples of the results will be shown in the next chapter. However, equation (4) presents a derivative of the function \( d(k,t) \) over time step \( \delta \) by Eulser's method as follows,

\[
y(t+h) = y(t) + hf(t,y) \text{ where } h \rightarrow \varepsilon \ \ldots \ldots \ldots \ldots \ldots (5)
\]

In place of a very infinitesimal time increments \( \varepsilon \), in (4) \( h \) is incremented by a series of finite time steps \( \delta \) that can be considered very small when compared to the large magnitude of total decay time. Thus equation (4) can be written in the above differential equivalent of equation (5),
The equation (6) can be solved more accurately using a popular numerical method Runge Kutta. A vector of \( d_i \)'s and \( K_i \)'s can be derived for each chain length from the time sequential derivatives of the general form,

\[
y(t_{i+1}) = y(t_i) + hf(t_i, y(t_i)) \quad \text{where} \quad K_i = hf(t_i, y(t_i))\]

\[
\text{y(t_i)'s representing d_i's can be derived by the above method for a number of equal increments of } h \text{ for a better prediction of the change in outcomes of the entire process trajectory from } t_i \rightarrow t_{i+n}. \text{ This is a very elaborate procedure, which is left for future research.}

5.4.2.1.4. A Continuous Model

A modified differential conversion of the equation (4) can be achieved if the probability function \( P(k, t) \) can be derived independently of the chain-length frequencies. In the above model, calculation of \( P(k, t) \) depends on the latter and so its cumulative distribution is of a Normal / Gaussian nature, the changes in the frequencies per each time unit affect the probability density calculation and cannot be ignored. However \( P(k, t) \) does not have to be a function of chain-length frequencies or normally distributed. This can be reconstructed as a fully separate function with any distribution such as Left hand skew or Right hand skew – some sort of \( \beta \) or \( \gamma \) or Weibull function, which are representative of non-normal distribution. The nature of the distribution can only be devised from the study of the experimental MWD data and from the pattern of the decay rates of different categories of the chain-length population. The latter has been studied in the current work and
will be described in "Method A Transition" in the next section. Secondly, the chain-length population set can be divided into a few finite subsets each can be assumed to consist of a constant average length or DP and thus can be regarded as constant for that particular subset. This way of cutting down variables would make it easier to deduce a differential equation in order to make the calculation method continuous and instant as well as cut down the load on the computer processing time. Thus the equation (4) can take the following general form.

\[
\int_{t=0}^{t=\delta} d(k,t+\delta) \cdot dk \cdot dt = + \int_{t=0}^{t=\delta} \int_{k=S_0}^{k=S_n} \left( \sum_{i=1}^{s_1} d(k,t) \cdot P(\phi,t) + \sum_{k=S_0}^{k=S_1} \frac{2P(\phi,t)}{k-1} \right) \cdot dt + \\
+ \int_{t=0}^{t=\delta} \int_{k=S_1}^{k=S_2} \left( \sum_{i=1}^{s_2} d(k,t) \cdot P(\phi,t) + \sum_{k=S_1}^{k=S_2} \frac{2P(\phi,t)}{k-1} \right) \cdot dt + \\
+ \int_{t=0}^{t=\delta} \int_{k=S_2}^{k=S_3} \left( \sum_{i=1}^{s_3} d(k,t) \cdot P(\phi,t) + \sum_{k=S_2}^{k=S_3} \frac{2P(\phi,t)}{k-1} \right) \cdot dt + \cdots 
\]

.................................................. (8)

\( P(\phi,t) \) \( \Rightarrow \) a function of \( \phi \) and \( t \) (a time segment of total time).

\( \phi \Rightarrow g(R_s, t) \Rightarrow \) a rate distribution function of the chain length subsets range \( (S_n - S_{n-1}) \), which is assumed to be constant for a small time segment \( dt \). \( \lambda_n (n=1,2,3,\ldots) \) are probability rate coefficients for finer adjustments of the equation, which may vary among the subset intervals and in between the consecutive time segments, but in general assumed as non-variable within the extent of a time segment. Life span of partial time intervals \( t \) (0 \( \rightarrow \delta \)) should be \( (t_i \rightarrow \delta_i) \) indicating \( i^{th} \) start point for each successive time segment \( \delta_i \), which can vary too (see equation 9).

\( P(\phi,t) \) refers to probability term allocated distinguishing the potential of reactivity for each molecular subset category within the range \( (S_n - S_{n-1}) \) that remains constant for a period of \( \delta_i \). \( \phi \) can be determined from the nature of decay rates of the polydisperse polymer subsets graded by their different sizes as observed from laboratory
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experimental data, assuming these rates vary with time and also with temperature and the atmospheric condition of the decay. For example in an electrical transformer in the power industry cellulose substrates insulator is immersed both in oil and air and the temperature can vary from 80°C-120°C. A simulation of this complex decaying environment in the accelerated lab-test reveals a non-linear overall kinetic rate that is dominated by the nature of both substrate structural complexity / regional access variability and environmental heterogeneity. This indicates that the temporal regional decay rates would not be equivalent and it is only practical to assume that in a real system, regional rates would follow some sort of non-linear distribution as demonstrated by the laboratory-accelerated tests. The equation (8) is more flexible than equation (4), which is restricted to simple decay models due to the probability function's dependence on both the individual and total chain-length frequencies. However, a non-linear kinetic relationship between time and overall resultant rate of average DP, revealed in the lab-test, indicates breaking rates for different chain sizes do not necessarily follow either any particular statistical (Normal) distribution nor maintain a similar pattern throughout the total temporal decay period until the average DP reaches a certain lower bound of 200 when decay becomes uniform. However, in the case of a slow partial decay process continuing for a large period of time (e.g. 10,000 - 20,000 hours) the nature of the decay process can be assumed to remain constant for smaller time segments comprising the latter. This would make the calculation instant and more flexible. Thus it is necessary to construct probability rates as independent of individual chain size frequency and only differentiating among the size domains rather than for each individual one. Thus equation (8) becomes not only more flexible but also amenable to adoption for complex decay phenomena. The flexibility can be further extended if the probability terms for the number and location of the bond breakage for a portion of time can be relaxed from any certain fixed values. This is denoted as a function \( \varphi(l,s) \) of the number of bonds contained in an average chain size \( l \) and the location \( s \) for the component subsets, that is considered in (8) to react within fixed boundary condition \( (S_i \rightarrow S_{i+1}) \). The whole is the resultant outcome of the sum of these
individual component reactions. Equally important is the consideration that once the boundary conditions of the time segments are exceeded then a new set of boundary conditions must apply. Note the probability terms concerning bond-splitting events in equation (9) are replaced with $\phi(t,s)$ functions that can be regarded as constant for the decay process operation during a particular time segment $\delta_1$, in the final equation (10).

Both the parameters $l$ and $s$ are not directly time dependent but rather depend on the choice of scission mode. Different modes may prevail in different pre-selected periods of the total decay time. This would help eliminate some of the rigidity of the pre-formed rules that are necessary to construct this algebraic statistical exact model. However, further work is required to make this instant calculation method work with a combination of more than one scission mode and hence attain the greater flexibility achieved in the computer Slider model technique (see section 5.4.1.3.)
5.4.3. **Markov Probability Matrix Method**

The simple mechanisms by which a polymer macro-chain system physically may split into two daughter fragments are described in chapter 2. However, the overall complex chemical mechanisms can be assumed to culminate from these simple concepts working in a complicated network connecting various models together in a random fashion. Occurrences of molecular events may appear to be random but are in fact influenced by their immediate prior decay state. Appropriate application of probability functions are essential to the efficient prediction of the extent of spread of degradation reaction zones over a time scale of partial decay long enough to cause irreversible damage. A suitable composition of probability vectors should be able to embody some of the environmental features, typical of a complex reactor system where exposure of different parts of the polymer substrate to the invasive attack is differently affected. As the extent of decay reaction proceeds, molecules experience transition from one state to another. A set of such probability vectors for each time series can be utilised to determine the amount and the direction of the speed of these transitions among each different region of the entire structural aggregate. The construction of the vector sets calls for a higher form of statistical approach. Thus a stochastic dynamic method has been adopted in this project by the use Markov statistics with the aid of computer techniques as follows:

1. Markov process and transition probability technique
2. Computer technique by means of Slider I and Slider II interfaces

How these techniques have been applied by means of mathematical modelling will be described in the following sections. An introduction to the Markov principle that is used in the model and sampling probability estimates for different subsets of molecular population is given in Appendix 5. The derivation of transition probabilities is described next.
5.4.4.1. Markov Chain Probability Principle

**Markov Chain and Random Walk Sampling:**

Markov sampling statistics have been devised in the current investigation on the basis of the following equation (Ross, 1997; Faires and Burden, 1998).

\[
x = f + Af + A^2 f + A^3 f + \ldots + A^m f = \sum_{n=0}^{\infty} A^m f
\]

The outcome of each random walk starting from a state \( i \) consists of the conditional probability products and the sum (see appendix 5 in section 5.4.3.1. for more details). The final \( W \) value is the one averaged over the walks that started at index \( i \) with its mean value given as,

\[
\bar{W} = \sum_{k, i} k \ldots p_{i_0 i_1} \ldots p_{i_{k-1} i_k} v_{i_0 i_1} \ldots v_{i_{k-1} i_k} f_{i_k} g_{i_k} \ldots
\]

The above concept has been utilised in deriving refined mean hourly values of MWDs of the cellulose material undergoing a partial decay procedures from sampling random walks to different categories of molecular chain states. The random walks represent the attributes pertaining to a scission operation.

5.4.3.2. Derivation of Transition Probabilities

Two different approaches have been tested to examine the potential for application of Markov principles (Metcalfe, 1997; Norris, 1997) in simulating cellulose decay.

**Method A.** Firstly, an easy method of derivation of transition probabilities is described for transition of polymer molecular states from most ordered to most disordered arrays. Compositional changes that may result as an outcome of the variable rates of the spread of degradation zones could be directly predicted from the experimental GPC data.
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Method B. The alternative route is to follow the fundamental principle in constructing Markov matrices of various categories of transition probabilities in the form of a random walk, allowing transition from anyone valid state to any of the rest of the defined valid states of the molecular process trajectory. The second method is obviously very laborious. How these two methods have been derived and implemented is described next through a numerical example.

5.4.3.2.1. Method A Transition

Step 1: Let frequencies at log(chain length x_i), at time t be f(x_i,t) = y_i. Choose two samples of x_i's from each of 6 subsets polymer chain population in descending order of chain size. Find their respective y_i's from the experimental data for each time segment to the final decay time. The frequencies are gradually changed due to fragmentations of longer chains.

Step 2: work out the variable degradation rates for different subset populations from their regression coefficients using the following formulae:

\[ \beta(x) = \frac{1}{n} \sum (t_i - \bar{t})(y_i - \bar{y}) \]
\[ \alpha(x) = \bar{y} - \beta(x) \bar{t} \]

Where \( y_i = \alpha(x_i) + \beta(x_i)t_i \) .................(24)

Step 3: Series of transition probabilities \( P_{x,t} \) can be constructed for \( x = \{0,1,2,\ldots,2000\} \), \( t = \{1,2,3,\ldots,50\ \text{hours}\} \), as an example:

\[ P_{x,t} \Rightarrow \begin{cases} \alpha_1 e^{-\beta_1 t} = c_1 & \text{if } x > 1500 \\ \alpha_2 e^{-\beta_2 t} = c_2 & \text{if } 1500 \geq x > 800 \\ \alpha_3 e^{-\beta_3 t} = c_3 & \text{if } 800 \geq x > 400 \\ \alpha_4 e^{-\beta_4 t} = c_4 & \text{if } x \leq 400 \end{cases} \]

Step 4: The above transition probability \( P_{x,t} \) ranges thus control the entire selection process of a chain subset type per unit time cycle. Each size belonging to a chosen type is considered equally probable.
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Step 6: The final cut is decided on the basis of chain type. For example, the middle position is preferred for the longest chains, an end-cut is allowed for the medium sizes. This can be controlled by of Slider II interface mechanism.

5.4.3.2.2. Method B Transition

Definition: Assume that the physical states of molecular decay process are a time dependent process and as such constantly change with the progress of time. Suppose the amount and the direction of these changes can be predicted in terms of some vectors which can be represented by a sequence of random variables

\[ X_0, X_1, X_2, \ldots, X_i, \ldots, X_N \]

where \( X_n \) is one of such state at time \( n \) such that the system can be interpreted to be in state \( i \) at time \( n \) if \( X_n = i \). Suppose there exists a set of possible values \( \{0, 1, \ldots, M\} \) that the above random variables may take that is only dependent on the immediate preceding state. The lab-experimental MWD data exhibited a pattern of progressive deformity from Normal distribution showing a virtual dependence on its immediate predecessor. Thus generation of evolution of chain distribution can form a perfect Markov chain sequence. Markov conditional probability matrices can predict the changes in the curve state. Each transient departure of the chain subsets from a state \( i \) to state \( j \) is dictated by conditional probability \( P_{ij} \).

For all \( i_0, \ldots, i_{n-1}, i, j \),

\[ P(X_{n+1} = j \mid X_n = i, X_{n-1} = i_{n-1}, \ldots, X_1 = i_1, X_0 = i_0) = P_{ij} \]

The transition probabilities of Markov chain represent the values of \( P_{ij} \),

\[ \{0 \leq i \leq M, 0 \leq j \leq N\} \forall P_{ij} \geq 0, \sum_{j=0}^{N} P_{ij} = 1, \{i = 0, 1, \ldots, M\} \]

It is convenient to arrange the transition probabilities \( P_{ij} \) in a square array or matrix of order \( M \times M \) as follows:
5.4.3.3. Analysis of Comparative Decay

In this case a three state Markov chain is conceived on the basis of degree of ordered composition. Suppose the entire polymer composition is assumed to initially contain highest proportion of ordered state with a mixture of disordered arrays of semicrystalline aggregates. Then the progression of decay may logically be assumed to impose conversion of crystalline regions into a semi-crystalline state and the latter into the amorphous or disordered state. For simplicity, imagine the ordered state is comprised of three categories of ordered states – highly ordered crystalline state containing longest chain molecules, the semi-ordered state of medium chain sizes and the disordered state of shortest chain sizes in physical terms. How Markov transition matrix can be composed with simplicity is exemplified next (cotton Linter in air at 120°C).

1) Three time points were chosen: Zero (0) hour (initial), 3648 hrs (intermediate), 5543 hrs (final)

2) The probability density function of ln(MW) was provided in the form of graphs (Heywood thesis, 1999)

3) \[ P(ln(MW)) \leq t = \int_{-a}^{x} g(x) dx \] , where \( g(x) \) is the probability function, is obtained by numerical integration. Values \( (x, g(x)) \) were obtained from the lab distribution graph. A mathematical software package was used to fit curves to the data.

4) The results are as follows:
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Zero (0) hr. \( y = k \exp(-69.99 + 24.53x - 2.15x^2), \quad 4.5 \leq x \leq 7 \)

3648 hrs. \( y = k' \exp(-38.72 + 15.72x - 1.61x^2), \quad 3.5 \leq x \leq 6.5 \)

5543 hrs. \( y = k'' \exp(-38.4 + 16.43x - 1.77x^2), \quad 3 \leq x \leq 6 \)

where \( x = \ln(MW) \), \( k, k', k'' \) constants for the required probability density functions. Quadrature formulae have been used to obtain the findings. The molecular lengths/sizes range are classified as:

\[
\ln(MW) < 4 \quad \text{as small} \\
4 \leq \ln(MW) \leq 6 \quad \text{as medium} \\
\ln(MW) > 6 \quad \text{as large}
\]

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Proportion of molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \ln(MW) &lt; 4 )</td>
</tr>
<tr>
<td>zero</td>
<td>0.0002</td>
</tr>
<tr>
<td>3648</td>
<td>0.0564</td>
</tr>
<tr>
<td>5543</td>
<td>0.1130</td>
</tr>
</tbody>
</table>

The above table shows that with time the proportion of large molecules decreases and that of the small molecules increases. The medium molecules first increase in number and then decrease.

An appropriate model for this would be through a branching process, which is a Markov Jump Process. The model involves decay rates on MW for defining the formation of three options of the breaking of longest molecule - one large and one small or one medium and one small molecule. Similarly, a medium molecule breaks into one medium and one small molecule or two small molecules. This leads to a complicated branching process and will require substantial additional work for analysis. This could be left for future
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investigation. An approximate model for the process that could be briefly investigated within the time limit of this project is as follows.

Consider a transition probability matrix $P$ which represents the transition probability from large to medium / large to small / medium to small etc. on an hourly basis. If recombination is ignored, then $P$ is the upper triangular.

\[
\begin{bmatrix}
B & M & S \\
B & X & Y & Z \\
P = M & 0 & P & Q \\
S & 0 & 0 & 1
\end{bmatrix}
\]

where, $X+Y+Z = 1$, $p+q = 1$

If $P^{3648}$ represents the transitional probability matrix for the transition from zero hr. to 3648 hrs and $P^{5543}$ represents that from zero hr. to 5543 hrs., then the proportion of molecules at 3648 hrs., would be $\Pi_0 P^{3648}$ where $\Pi_0 \Rightarrow$ gives proportion of large, medium, small at 0 hrs. $\Pi_0 P^{5543} \Rightarrow$ the proportion of molecules at 5543 hrs.

The equation $\Pi_0 P^{5543} = \Pi_0 P^{3648}$ can predict the relative proportion of the different segments of the total polymer chain population on the basis of their size at the end of time interval 3608 hrs., provided those at the start of decay are known. So the general equation is given,

\[
\Pi_t = \Pi_t P^i \text{..................(26)}
\]

Where $t_k$ represents a $k^{th}$ time state of population and $t_i$ a starting time $i$ as the zero$^{th}$ time state ($i=0,1,2,\ldots$).

This would also help in predicting or analysing their comparative decay rates. The equation can be solved from the above by matrix multiplication for the required number of hours, if the transitional probabilities $X$, $Y$, $Z$, $p$ and $q$ can
be determined. The latter could be calculated from the lab experimental data with some further assumptions.

5.4.3.4. Hourly Calculation of MWD

It is essential to imagine that the physical system is composed of a wide range of states. Ideally the transition probabilities should be determined for each chain length to reduce to the shorter chain lengths at any time $t$. Lowry (1970) showed how to obtain a Markov chain transition matrix to calculate PCLD for polymerisation. In this case of step growth polymerisation, each sequential chain growth for a number of already formed chains at any time $t$ is regarded as a Markov process. For a given extent of reaction a growing chain at a certain position is regarded as a transient state and whether it grows further depends on availability of a monomer in that position and the transition probabilities. Transition probability is regarded as zero if such reaction (transition) between a particular pair of monomers (transient states) is forbidden. But this would be very tedious and time-consuming task.

A Markov transition probability matrix was composed in a similar but more simplified way to the present case of depolymerisation. Here the chain dimensions at the start of the decay constitute the transient states. Suppose a state $i$ presumes a dimension of $I$ that can break into any of the chain sizes from the next highest to the allowable lowest dimension. Hence the stochastic matrix $P$ will be of $M$ degree according to $M$ number of transient states (chain-lengths) and hence will be $M \times M$ dimension. Suppose a chain of size $l_i$ in the distribution can be one of the transient states $A_1, A_2 \ldots A_n$ provided $n < i$ at any time $t_1$ during the decay process. The decomposition reaction that may alter the state of this length to any of the other states (reduced sizes) depends on the respective transition probabilities. Once a chain-length state is altered to any of the transient state, it also alters the relative frequency of that state (chain-length) as it divides into some percentage. It thus contributes to the frequency of different chain states, which are smaller or equal to that chain length. The state change to higher chain size is considered invalid or forbidden and hence the transition
probabilities are regarded as zero. Similarly a permissible lower limit to the size of the broken fragment can be imposed, those can be regarded volatilised out of the system. This depends also on the temperature. A terminating or absorbing state is considered as the limiting DP which length (state) cannot reach from any of the transient states.

For Markov chains, the probability of passing to some state $A_i$ depends only on the previous state of the entire system and does not depend on what its states were at earlier times. Here the entire chain length distribution changing with time $t_1$, $t_2$, $t_3$, $t_4$ $...........t_n$ is also considered as a Markov process. Thus if the chain distribution is known at a certain hour the same could be predicted and calculated for the next hour by means of a transition matrix as follows.

\[
\Pi_l = \Pi_0 P^l \text{ where } \Pi_l \text{ refers to a } M \times 1 \text{ matrix of proportion of certain chain-lengths at } l^{th} \text{ hour, } l=0,1,2 \ldots \ldots m
\]

\[
\Pi_1 = \Pi_0 P^1 
\]

\[
\Pi_2 = \Pi_0 P^2 
\]

\[
\Pi_3 = \Pi_0 P^3 
\]

\vdots 

\[
\Pi_m = \Pi_0 P^m \text{ .......... .......... .......... .......(29)}
\]

\[
\Pi_m \Rightarrow \text{Yields the desired polymer chain-size concentration at m}^{th} \text{ time of the decay process required to construct the polymer chain-length or MW distribution. The former can be obtained by solving equation (26) through the set of equations starting from (28) to (29) for m time steps. This requires the initial zero and 1 hour concentrations for the ease of constructing the unknown transition probability matrix } P. \text{ However, this process gets more complicated as } m \text{ increases, since it involves } m \text{ time matrix multiplication. For testing this method in the case of cellulose the difficulty was faced as hour 1 data were not there since } \Pi_m \text{'s are only obtained from the accelerated lab test data for certain hours with long gaps in between. The} 
\]
testing times are for example in the following order for decaying cotton linter in air at 120°C – where $t_i$’s are: $t_0=0h$, $t_1=20.75h$, $t_2=52.5h$, $t_3=185.5h$, $t_4=357.75h$, $t_5=1368h$, $t_6=2448h$, $t_7=5543h$. The above does not give MWD data for hour 1. This difficulty was overcome by using an interpolation method Newton’s divided difference formula (details in appendix 5). A brief account of the stages of development to derive the final simplistic method is given below.

1. Geometric or Flory’s most probable distribution was used in the case of polymerisation. This was modified to suit depolymerisation and the transition probabilities constructed. For an example, if $p$ represents success for a chain breaking i.e. breaking of one bond and $(1-p)$ stands for failure to break a bond, then probabilities for a bond to break at $i^{th}$ position from a chain of length $j$ can be calculated as follows, ($i = 1, 2, 3, \ldots \ldots j-1$)

$$P_j = p'(1-p)^{j-i} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (33)$$

2. The equation (33) was tested to deduce the desired transition probabilities where breaking probability $p$ can be assumed equal for all chain-lengths. However, this did not produce a desirable result for a cellulose substrate, as this yields probability values for fully random events and also biased towards the longest chain length to break. In the case of cellulose the breaking pattern varies indeterminately within the chain subsets as well as with time. So the outcome resulted in a very skewed set of curves.

3. Alternatively, one can try to construct separate sets of preferential transition probability matrices for each separate time segment which would be biased to either medium or largest size in order to reproduce the simulated MWD close to the lab test ones. A percentage chain breaking mechanism can also be adopted from the equation (33).

4. However, the use of equation (33) to derive the effective transition probabilities by either method stated above seems to be not very suitable in
Chapter 5: Mathematical Models

the case of cellulose decay simulation. Hence the following steps were taken to derive these from the study of the experimental data:

1. Equation (22), (23) and (24) are used to derive the individual rates $Y_i$ for each chain length.

2. A series of $Y_i$ were selected for each of six subset of the entire molecular population via a random sampling procedure and $P_{ij}$ s are constructed from the average sampled $Y_i$ and $V_i$ vectors following equations (14), (15), (16) (given in appendix 5).

3. Two sets of matrices were derived – $A$-matrix (to cater for the rates at which new generation of broken fragments join the existing molecular population) and $B$-matrix (to cater for the rates at which the parent chains are broken and thus to be discarded) on the basis of the principles of sampling procedure described earlier.

4. The Newton’s divided difference formula was used to construct MWD curve for 1 hour from the zero hour in order to obtain $\Pi_{ti}$ values to utilise equation (29). In this way the huge number of Matrix multiplication can be reduced to a few.

5. The Newton’s divided difference formula can also be used to obtain any of the intermediate time MWD curve data to obtain $\Pi_{t_{i-1}}$ frequency matrix corresponding to i-1th hour. The later can be treated as zeroth hour to begin a random walk that starts at time i-1th hour to traverse through the next set of hours until it reaches a certain (k-i)th hours of interval, before the walk converges following equation (21).

6. Using equation (29) the desired frequencies $\Pi_{t_i}$ matrices were obtained from which the hourly MWD curves were reconstructed for the corresponding sequential hours from i to k.

7. Finally equations (18-20) were used to obtain an averaged value of the random walk sampling on any (i-k) hourly interval that consists of visiting from ith state to kth hourly state of the entire system existence.
This would provide more refined average MWD curve for a particular extent of time, but not hourly curve data.

5.5. Simulated Time Models

There is no direct way to convert or deduce real time directly in the case of computer simulated polymer degradation experiments. One can keep a log of computer runtime of a simulation model run and treat computer time as an indicator of real time. But practically this approach gives falsified information, as computer time is entirely processor performance based and hence vastly dependent on the number of tasks the operating system is currently handling. Ideally, time progression of degradation can only be truly monitored from the number of bonds breaking per unit time or per each reaction extent. The Emsley and Heywood (2000) equation for non-linear decays suffers from the problem that beyond a certain value the equation exponents become infinite or not valid. In order to avoid this problem other statistical distribution methods (such as classical Poisson) were investigated. The following four methods have been investigated for mathematical modelling of simulation time:

(a) Exponential distribution of simulated time (in hours)
(b) Poisson distribution of simulated inner cycles (in hours)
(c) Using a derivative of rectangular hyperbolic function
(d) Random Geometric distribution

The concepts are included in Chapter 7.

5.5. Smoothing Functions

The relationship between independent and dependent variables and parameters is represented in the form of a function or via set mathematical equations. A smooth and continuous representation of the variables in a physical problem is important especially in cases where graph contour and
shape contributes to characterization of the problem. Various curve functions are useful in object modelling and other graphical applications. Displays of these curve paths can be generated either directly from explicit representations — "\( Y = f(X) \)" or from parametric forms or incremental midpoint method to plot the curve using the implicit functions "\( f(X,Y) = 0 \)". For drawing curves segments, a non-linear least squares approach can be adopted with the use of some approximating functions, usually polynomials. A polynomial function of nth degree in X can be represented as

\[
Y = \sum_{k=0}^{n} a_k X^k = a_0 + a_1 X + \ldots + a_{n-1} X^{n-1} + a_n X^n
\]

Where \( n \) = a positive integer, \( a_k \) = constants with \( a_n \neq 0 \).

Polynomials are useful in a variety of graphic applications including designing object shapes. In preserving curve contour, shapes and features, inclination of data paths are followed by specifying a few points to define the general contour and then fitting the selected points with a polynomial. One of the most efficient ways of curve fitting is accomplished by means of constructing cubic polynomial curve sections between each pair of specified points. The end outcome of joining the polynomial pieces is a continuous smooth curve. The latter is known as a spline curve or cubic spline. There are various spline-generating methods to set up spline curves. Cubic Spline Interpolation method (Spath, 1995) is implemented in this project graphical smoothing routine. The general form of a cubic interpolant \( S \) is used

\[
S_j(X) = a_j + b_j(X - X_j) + c_j(X - X_j)^2 + d_j(X - X_j)^3
\]

for each \( j = 0, 1, \ldots, n-1 \). See appendix 5 section 5.10.3 and 5.10.3.2 for more details.
5.6. Conclusions

- Early investigations in this issue used mathematical calculations that lead to complicated painstaking derivation of equations using simple statistics and assuming mono-disperse system.

- Nanda and Pathria (1959a-d) investigated the process of fragmentation in a more innovative way, using combinatorial mathematics and number theory to deduce the ultimate probable number and sizes of chain dissociation products in different reaction situations. These mathematicians were the first to introduce more sophisticated and realistic ways to deal with polydisperse system.

- At a later stage the numerical analysis techniques were enhanced in the areas of commercialized polymer synthesis introducing a more direct approach where time dependent gradual polymerisation was conceived as classical Markov or Poisson process (Laurence et al., 1988).

- A number of problems are associated with iterative Monte Carlo simulation modelling method to obtain clear graphical features of temporal intermediate MWD curve sequence as close to those obtained from GPC due to its inherent random nature and massive number of repetitive cycles to carry out simple arithmetical estimates of the degraded fragments. This unnecessary extends the CPU time.

- Instead of calculating an averaging value through a long series of repetitive trials, the goal can be reached more directly through a mathematical expression that can harness simple algebraic formulae applying the principles of induction methods and exact statistics. The concept for transformation of iterative to non-iterative function was demonstrated through a simple coin tossing analogy.

- This chapter investigated if the above novel concept can be ideally applicable in depolymerisation processes using more direct approach in contrast to Monte Carlo Iterative. Chapter 6 will demonstrate the desired results in reproducing decayed MWD trends.
Algebraic exact methods constitute one of the direct approaches that were originally formulated for discrete processes and included a separate formulation to represent each scission process. These were compared with their iterative counterpart to find if they resemble one another or not. The direct algorithm produced more stable, smooth curves with clear images and finer detailed features of the distribution curves than the iterative algorithm.

Improving the probability density function and making it independent to the chain frequencies of a polydisperse polymer system further improved the Algebraic exact statistics method from a semi-continuous to a continuous form. The latter requires further optimisation and extension to incorporate all different scission mechanisms into one expression and can be regarded as further future project. In addition this method can be further explored to other polymer systems apart from cellulose, studied in the present project.

A suitable composition of probability vectors as mentioned above was achieved by means of Markov chain transition probability matrices. The method a and b transitions were deduced in respect of applying a random walk strategy to the entire reactive molecular species. The changing dynamics of the latter were imagined as history independent chain states.

Introducing computer interface strategies Slider I and II enhanced the Monte Carlo iterative model further. The former samples a random quantity from sequentially weighted polymer reactive zones imagined as an infinitely large system. The latter samples a random quantity from a finite range of selected reactive zones where extents of reaction proliferation solely depend on the respective weights.

The two PDF methods are kernels to the above model – triangular and rectangular schemes.

All three models were designed to embody complex reactor environmental features and complex scission strategies.
Chapter 6

Simulation Results from Mathematical Models

6.1. Introduction

6.2. Statistical Methods
   6.2.1. Outcome Hypothesis
      6.2.1.1. Reactions in Oil
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6.3. Statistically Selected Results
   6.3.1. Examples of MWD Trends
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6.6. Conclusions
Chapter 6: Simulation Results

6.1. Introduction

This chapter presents the simulation experimentation results in relation to temporal changes in MWD curves, the related moments and other moment-derived parameters for different temperatures. The mathematical models (described in chapter 5) were used. The simulated results provide a means of identifying possible molecular events that takes place in a complex degradation process. The partial temporal degradation patterns of cellulose in different environmental conditions, obtained from the lab experimental test were used as a basis for comparison. The environmental attributes (Air, Oil, Vacuum) at three different temperatures (120°C, 140°C, 160°C) were parameterised in the program interfaces and dialogue boxes (Illustrated in Chapter 4). The differential rates of nucleation and spread of reaction zones were simulated by means of probability structures (see Slider I and II interfaces in Ch 4 and models in Ch 5). The representative selection of reaction conditions was tested statistically to find the closest match of the MWD curves to lab-test results and the effects of temperature, oxygen and water were investigated.

A quantitative analysis of cellulose kinetics is given in Chapter 7, together with a scheme of prediction of polymer durability from simulated data.

6.2. Statistical Methods

55-60 Slider model simulation experiments were carried out using different combinations of the 6 different scission events and the following. MWD time curve physical characteristics were calculated: mean, median, sigma, beta2, area of each time curve, peak height etc., plus moment related characteristics such as polydispersity, delta, variance and dispersion etc. Sets of co-linearity test were carried out comparing any two characteristics for all of them. The results were compared with the same data from lab-test curves. Then two sets of these 55-60 Rho values were plotted against the sample categories with lab-test as the mean (Figures A6.1a-i and A6.2a-j,
given in appendix 6), in order to find which samples display closest values of the various attributes to those of lab-tests. This preliminary analysis helped to indicate the closest attributes between theoretical (simulation) and experimental (i.e. lab-test) data and reject those that do not match, reducing the choice to 2 or 3 sample combinations. The following samples were chosen as the closest possibilities to the probable scission events that may take place during cellulose degradation.

2. Cutlength – Cutpercent – Cutchop (marked as Len-Pct-Chop).

Chi-square test was used to find more precise combinations as follows.

(a) 10-15 runs were done for each of the above samples – keeping the event combination and their percent and ranks constant and only varying the Slider II parameters.

(b) Where physical attributes from the Rho tests above were found collinear only one of the two was selected the other was eliminated.

(c) Next the values of these attributes for each separate time segment for each sample were then collected and a set of chi-square distribution were performed to 6/7 degrees of freedom depending on the number of chosen attributes for each of the above 3 primary chosen combinations.

(d) The levels of significance were then deduced from the statistical table. The former values indicated which samples are significantly different to the lab-test one and which are not.

The above was performed on 120°C oil data as mean. This was used as the basis to find the closest match for the other two temperatures for cellulose decay simulation experiments. More details of the method and corresponding results are given in Appendix 6 (sections A6.2-A6.3.3.). The latter also contains the related graphical plots (Figures A6.1a-i and A6.2a-j).
Chapter 6: Simulation Results

concerning primary selection of the scission event combinations and Chi-square test result data (Tables A6.1-6) and the tables of the acquired hypothesis from the same (Tables A6.7-8) to lead to more specific molecular details. The above statistical tables were shown to adequately demonstrate postulation of occurrences of most probable reaction strategies in oil (Table A6.7) and air (Table A6.8) and their relative dependences on medium and temperatures. These tables are also presented in this chapter and briefly described in the following section.

6.2.1. Outcome Hypothesis

Tables of hypothesis (H₀/H₁) integrating all environments for both media - oil (Table 6.7) and air (Tables 6.8) were drawn out as outcome of the \( \chi^2 \) test data with a view to provide a more detailed assessment of the outcomes. Chi-square tests aim to satisfy either of the following two hypotheses.

\[ H₀ : \text{The simulated samples (i.e. observed) are significantly different} \]
\[ \quad \text{from the corresponding lab-test ones (i.e. expected).} \]

\[ H₁ : \text{The simulated samples (i.e. observed) are not significantly} \]
\[ \quad \text{different from the corresponding lab-test ones (i.e. expected).} \]

The hypothesis \( H₀ \) is marked as 'significant' and \( H₁ \) as 'not significant' in the above tables.

Total decay time was sectioned into three phases namely early, mid and late decay. The statistical end results thus enabled a view of precedence of a particular molecular event (from the previously selected three) depending on which hypothesis it satisfies for a particular case (i.e. reaction environment). The data obtained from the above two tables, finally lead to a view of the overall nature of reaction strategies that predominate with changing temperature and the advancement of decay.
Table 6.7: represents postulated hypothesis from Chi-square statistical tests, used to detect specific combination of scission events responsible for cellulose substrate decay in oil.

<table>
<thead>
<tr>
<th>Decay Phase</th>
<th>Curpercent+Wklink+Unzip</th>
<th>Cutlength+Weaklink+Unzip</th>
<th>Cutpercent+Cutlength+Cutchop</th>
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<td><strong>Late</strong></td>
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Table 6.8: represents postulated hypothesis from Chi-square statistical tests, used to detect specific combination of scission events responsible for cellulose substrate decay in air

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<th>Cutlength+Weaklink+Unzip</th>
<th>Cutpercent+Cutlength+Cutchop</th>
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</tbody>
</table>

157b
Chapter 6: Simulation Results

The following observations were statistically discerned.

6.2.1.1. Reactions in Oil

During the early decay phase the event combination number 3 (i.e. Cutpercent + Weaklink + Unzip) appears to be most predominant independent of temperature rise, but event combination number 2 (i.e. Cutlength + Cutpercent + Cutchop) seems to compete with 3, specifically at 140°C.

During the mid decay phase the same mechanism (i.e. number 3) appears to continue with stronger competitive interference from the event combination 2 reactions, specifically at 140°C and 160°C.

During the more advanced (end) phase of decay, mechanism 3 appears to tail off and be succeeded by either of mechanisms - 1 (i.e. Cutlength + Weaklink + Unzip) or 2.

Mechanism 1 appears to be significantly less probable in oil than mechanism 3, independent of temperature. However the interference from mechanism 2 may become more persistent with rising temperature as well as with extent of decay.

6.2.1.2. Reactions in Air

Mechanism 1 (i.e. Cutlength + Weaklink + Unzip) appears to take precedence over the other two during the early decay phase, particularly at 120°C and 160°C, with competition from mechanism 3 (i.e. Cutpercent + Weaklink + Unzip) at moderate temperatures (120°C and 140°C).

During mid decay phase mechanism 3 appears to dominate, indicating a preferential percent chop from the chain ends rather than the restricted fixed length cut, particularly at the two extreme temperatures (120°C and 160°C).
Mechanism 1 appears to regain control during late phase of decay, leading to a more directional molecular decay and imposing a certain ordered manner of end chopping events specifically at 120°C. There may be some small interference from mechanism 1 at 160°C and mechanism 2 at 140°C.

The strength of competition from mechanism 2 appears to be significantly greater in the earliest decay phase and at lowest temperatures (i.e. lower than or equal to 120°C). It appears to persist until the end of the mid phase, when it tails off. However at 140°C, mechanism 2 seems to recommence in the later stages of decay.

### 6.3. Statistically Selected Results

Slider I interface parameters symbolise the type of invasion i.e. reaction events and their degree and order of occurrences with the progress of time. Slider II interface parameters are designed to integrate reaction intensity and these can vary in different time segments. Thus a competition between two or more different modes of scission reactions or reagent attack or their parallel simultaneous occurrences signifying an event can be mimicked. Different combination and strength of these events would yield different MWD results. The statistically selected "best fit" MWD decayed curves derived from simulation experiment are presented in the figures 6.1a to 6.10a and associated results in Tables 6.9 a-c to Tables 6.18 a-c and figures 6.1b-c to 6.10b-c in the next few pages with the description of the curve-trends.

Parameter tables for the Slider I and II for each of the ten trends (1-10) are given in Tables 6.9 a-c--Tables 6.18 a-c respectively. The tables display the user (i.e. myself in this research work) chosen various scission and kinetic parameter values used in the experimentation such as (a) Slider I combination of events and their percentages, (b) the Slider II parameters and probability weight charts and (c) Slider I event’s ranks for separate time cycles. Their graphical representations are given in Fig. 6.1b-c to 6.10b-c.
Fig 6.1a
Trend1 MWD

Fig. 6.2a
Trend2 MWD
Table 6.9a-c: Slider I and II Parameter Tables for Trend 1

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### Table 6.10a-c: Slider I and II Parameter Tables for Trend 2

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<th>Percentcut</th>
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</table>
Chapter 6: Simulation Results

Set and Actual Occurrences of Scission Events for Trend 1 (Fig. 6.1b-c) & Trend 2 (Fig. 6.2b-c)

Trend 1

Trend 2
Fig. 6.1b-6.10b illustrates set occurrences of events and 6.1c-6.10c illustrates actual occurrences of events over the total decay period.

6.3.1. **Examples of MWD Trends**

*(Figures 6.1a-c--6.10a-c & Tables 6.9a-c-- 6.18a-c)*

Let's consider the GPC generated curve-sets for all 3 temperatures (120°C, 140°C, 160°C) in oil. The overall curve shift patterns follow the same trend — loss of height at the early decay stage, broadening of peaks, irregularities and curve deformation that appear during the advanced stage of decay. By the end stage as the curve shifts towards the lower molecular range, it regains height and sharpness and the curve regains a balanced Gaussian form. Significant differences lie with the speed of shift. For example, the loss of peak height occurs within 13 hours at 160°C and 24 hours at 120°C. Any moderate amount of curve shift observable from the onset of decay, takes 1872 hours at 120°C, 73.5 hours at 140°C and only 24.5 hours at 160°C.

Trend 1 (Fig. 6.1a): Combines Cutlength, Cutpercent and Cutchop scission modes.

A typical bimodal pattern emerged during the first phase of decay with loss of height. During the middle phase peak broadening and deformities appeared. This is due to a high degree of end chopping into a wide variety of sizes affected by a competition between the first two scission modes. In the more advanced stage of decay, Cutchop initiated rapid partial unzipping of the longer fractions and thus enabled the regain of a regular shaped normalised sharp distribution.

Trend 2 (Fig. 6.2a): Combines Cutlength, Weaklink and Unzip scission modes.

Like the above trend, the initial stage generated bimodality. This reflects a parallel performance of Unzip and Weaklink modes, where particular size of fractions generated by weaker links are further zipped away by the action of Unzip giving rise to two kinds of main fraction peaks. Further invasion into
Chapter 6: Simulation Results

Fig 6.3a
Trend 3 MWD

Fig 6.4a
Trend 4 MWD

Trend 3 MWD

Trend 4 MWD

160a
**Table 6.11a-c: Slider I and II Parameter Tables for Trend 3**

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### Table 6.12a-c: Slider I and II Parameter Tables for Trend 4

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### Diagrams

*Diagram a and b showing Cycle Times and Weaklink Endpoints.*
Chapter 6: Simulation Results

Set and Actual Occurrences of Scission Events for Trend 3 (Fig. 6.3b-c) & Trend 4 (Fig. 6.4b-c)
crystalline regions and hence the chopping of the longest molecules by the action of both Cutlength and Weaklink accumulated more differential sized fractions. The result was a peak broadening effect, which sharpened again by the more rapid unzipping that cut down large differences in sizes in the new generations. The curve sharpening was more accentuated in this trend in comparison to the previous trend.

Trend 3 (Fig. 6.3a): Combines Cut-in-half, Weaklink and Unzip scission modes.
This trend differed from the above two in generating a trimodal curve in the earlier decay phase. This reflects the action of Cut-in-half mode that apparently predominates in the upper middle to longest chain (i.e. crystalline) regions. The other distinct feature was that, as the competition of other modes increased, and the nucleation centres spread with time, so the extreme right hand peak of the trimodal curve started to diminish slowly in the longest MW region. This indicates slow deterioration of the most ordered crystalline regions and took over 12,000 hours to complete. Unzip was activated after 1060 hours in order to regenerate an ideal sharp Gaussian type curve in the end unlike the above two.

Trend 4 (Fig. 6.4a): Combines Cut-in-half, Weaklink, Cutpercent and Unzip scission modes.
This trend displayed a unique pattern of curve shift due to competition between four varieties of modes. A high number of reaction zones, clustered in the longest chain range, induced a much faster spread of decay and curve shift. The shift to the middle chain length region occurs within 816 hours with regain of peak height and regularity of the shifted curves. Note the significant features of multi-modality at the early stages are absent despite the inclusion of Cut-in-half scission. This is due to the introduction of a higher percentage of Unzip. The faster degradation of the longest molecules enabled chopping and unzipping through out the entire reaction regions at almost equal rates. As a result the curve shifts towards the LMW region keeping equal peak heights.
Chapter 6: Simulation Results

Fig 6.5a
Trend5 MWD

Fig 6.6a
Trend6 MWD
## Table 6.13a-c: Slider I and II Parameter Tables for Trend 5

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### Table 6.14a-c: Slider I and II Parameter Tables for Trend 6

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#### b) 161c
Set and Actual Occurrences of Scission Events for Trend 5 (Fig. 6.5b-c) & Trend 6 (Fig. 6.6b-c)
Chapter 6: Simulation Results

Trend 5 (Fig. 6.5a): Combines Cutpercent, Unzip and Weaklink scission modes.
This trend exhibited the distinct bimodal characteristics in the first three decay curves that were observed in trend 1 and 2. This resulted from a parallel progression of Weaklink and Unzip reactions, lasting to 1173 hours from the onset of decay. Bimodality was disrupted by incorporation of Cutpercent that affected peak broadening in the intermediate stage and by 9331 hours time peak height was restored but broadness was not diminished. This may be a reflection of the unequal spread of reaction centres and unzipping.

Trend 6 (Fig. 6.6a): Combines Cutpercent, Cutchop, Unzip and Weaklink scission modes, where occurrences of the middle two are highest and parallel and the other two compete with each other.
A continuous flow of smaller size fractions was maintained throughout the total decay as reflected in the production of a series of broad round shaped curves in the subsequent generations. The broad bimodal curves in the early time (0h-1173hrs) revealed the accumulation of two sets of fractions - upper and lower middle length chains, indicating rapid mobilisation of semi-crystalline reaction nucleation centres. Note the curve deformity was not pronounced in this trend, possibly because both Unzip and Cutchop annihilate the small fractions in the advanced decay stages.

Trend 7 (Fig. 6.7a): Combines Cutpercent, Cutchop and Weaklink scission modes presenting, in contrast to the above trend, a more deformed curve set with shoulders on either sides. This is probably due to the absence of Unzip mode that helps cutting down the breath in size distribution and accumulation of smaller fractions.

Trend 8 (Fig. 6.8a): Combines Cutchop, Cutlength, Cutpercent, Weaklink and Unzip scissions.
Combination of five scission modes generated a set of MWD curves with sharper unimodal peaks and the absence of deformities or shoulders. In the early phase, high rate of Cutchop was activated with simultaneous reactions
Chapter 6: Simulation Results

Fig 6.7a
Trend 7 MWD

Fig 6.8a
Trend 8 MWD
Table 6.15a-c: Slider I and II Parameter Tables for Trend 7

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162b
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Set and Actual Occurrences of Scission Events for Trend 7 (Fig. 6.7b-c) & Trend 8 (Fig. 6.8b-c)
of Cutlength and Weaklink type of scissions. The latter two yielded very small sized fractions from the upper medium length chains in the early to middle phase. Accumulation of a fixed sized species generated unimodal sharp peaks as opposed to bi/tri-modal curves observed in the most cases with no peak broadening or deformed features. Unzip and Cutpercent were replaced with Cutlength and Cutchop in the later phases, while Weaklink scission was allowed to continue. This reaction strategy spread new reaction zones vigorously through the polymer and minimised the increase in the breadth of dissimilar sizes as the decay progressed.

Trend 9 (Fig. 6.9a): Combines Cut-in-half, Cutpercent and Unzip scissions. As apparent in the figure, a multi-modal (i.e. mostly tri-modal) feature emerged that is distinctive of Cut-in-half in the longest chain region that prevailed from the start to middle time interval. This disappeared with the introduction of high degree of unzipping and turning off the Cut-in-half scission mechanism.

Trend 10 (Fig. 6.10a): Combines Cutlength, Cutpercent, Unzip and Weaklink scissions. This combination created a set of deformed MWD curves of broad distribution unlike the trend 9. Allowing a wide variation in the end-cut, percent cut and percent to unzip at different time cycle caused this effect. In the early decay phase equal proportions of Weaklink cleavage and Cutlength scission produced a wide variety of sizes, which were unzipped at differing rates with domination in the semi-crystal (medium length chain) regions, causing loss in heights for the most part of the decay phase.

### 6.3.1.1. MWD Trend Comparison

One of the special features of the above-simulated MWD trends, basically designed to suit cellulose experimental GPC results (Emsley and Heywood, 2000 and Heywood's Thesis, 1997), is intermediate bimodality. This feature is displayed more prominently by almost all trends except 3, 4 and 8. Bimodality in the intermediate phase shifts is more common in bio-
Chapter 6: Simulation Results

Fig. 6.9a Trend MWD

Fig. 6.10a Trend MWD
Table 6.17a-c: Slider I and II Parameter Tables for Trend 9

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Set and Actual Occurrences of Scission Events for Trend 9 (Fig. 6.9b-c) & Trend 10 (Fig. 6.10b-c)
macromolecules such as Chitosan degradation (Boryniec et al., 1997) by enzymic, hydrolytic and ionising radiation (Fig.2.9a-c). Similar bimodal trend has been displayed by a number of multi-stranded polysaccharides (see Chapter 2) such as duplex of Xylan, triplex of Scleroglucan and Pollulan (Stokke and Christensen, 1992-1996 and Hjerde et al., 1997-1999). In some densely built or branched chain synthetic polymers bimodal shift patterns are also evident by their intermediate molecular states during degradation or synthesis such as LDPE (Pladis and Kiparissides, 1998), multistage polymerisation of Poly-olefins (Zacca et al., 1997) and some others when only subjected to mechanically induced degradation (Flora, 1993; Price and Smith, 1991). In these cases preferential scissions yield two categories of product chain fragments, enforcing the preceding peak split into two.

However in the case of bio-macromolecules, bimodality can be affected from variety of reasons such as preferential cleavage based on two different regions, two competing or parallel reactions in the same or separate locations, differential reaction speed and participations due to structural complexity. The latter is shown to be one of the key reasons in generating bimodality (Liu et al, 1998; Shaw and Tuminello, 1994). For example branch distribution correlated with thermal behaviour in a variety of high-density polyethylene tend to fluctuate between unimodal to bimodal molecular weight distribution (Kim et al., 1996). Multi-modality is commonly exhibited by broad polydisperse polymers due to polymeric network formation via generation of cross-linking (Tobita, 1994-98). Catalytic polymerisation of polyethylene displays a range of shape changes of the intermediate MWD curves from bimodal to multi-modal in variable environmental conditions (Mori et al., 1998). In the present simulation study, multi-modality is exhibited by trends 3 and 9 where Cut-in-Half mechanism predominates in the crystalline regions in competition with other end-chopping mechanisms.

The other features such as long tail end in the HMW region as displayed by trends 3, 5, 8 and 10 are quite unique in some synthetic polymers such as PCT1, low-density polyethylene and polypropylene (see Fig. 3.25a-d in Chapter 3). HMW tails are also observed in Chitin degradation by ionising
radiation. Unimodal consistent lateral shifts without displaying much noticeable curve / peak deformity are observed in some modified derivatives of synthetic polymers such as SKS30 (Fig. 3.25a-d) (Yanchuk et al., 1990), peroxide promoted polypropylene degradation (Huang et al., 1995; Tzoganakis et al., 1988) and in degradation of PVC (Malac, 1971). This is exhibited uniquely by trend 8, where combined action of 5 different scission mechanisms cuts down the extent of polydispersity and multiplicity or broadening of intermediate peaks. This strategy resulted in an end outcome similar to random degradation as displayed in Chitosan degraded via ionising radiation, where all molecules were exposed equivalently to the degradative agents. The ratio of end-cleavage to unzip can be an important MWD curve-shape controlling parameter. This will be tested later.

6.3.2. Relationship Between Physical Molecularity And Kinetics of the Trends (Fig. 6.1d-6.10h)

The previous section endeavours to present a more detailed account of the molecular mechanisms from the observation of the MWD curve statistics. However, a general overview of the order of reaction kinetics can be only ascertained from the relationship between the moments of polymer chain size distribution (PCLD) and the weight and number averages (i.e. Mw and Mn). The figures 6.1b-6.10h given in the next few pages thus help to unravel more about relationship between MWD and PCLD. Physical significance can be attached to the lower moments of PCLD. For example the zeroth moment (μ₀) represents the total molar concentration of the polymer, the first moment (μ₁) - the total number of bonds present per volume and the second moment (μ₂) - the weighted sum of the number of molecules present per volume in the entire polymer population. DPn, DPw and DPz are various average degrees of polymerisation specified solely in terms of various moment ratios as below.

Average Mn = Mass of monomer * Average DPn ( = μ₁/μ₀ )
Average Mw = Mass of monomer * Average DPw ( = μ₂/μ₁ )
Average $M_z = \text{Mass of monomer} \times \text{Average } DP_z = \mu_3 / \mu_2$

The other parameters such as Polydispersity ($Q$), Variance ($\sigma$), Delta ($\Delta$) and Dispersion ($\delta$) are used to measure statistically the combined effects of the polarity of the reactions and their physical significance. For example, Polydispersity ($Q$) gives a direct measure of the breadth of molecular weight size, Variance ($\sigma$) is the statistical mean of the latter and is related to the second moment about the mean. The most useful property of the PCLD is the precise magnitude of $Q$, and $M_n$ that may vary in an obscure manner throughout the long period of a slow partial decay phenomenon. Finally, Dispersion ($\delta$) represents the difference between $M_w$ and $M_n$ and Delta ($\Delta$) provides a fraction of the number average degree of polymerisation by one standard deviation. Their mathematical relationships are given below.

\begin{align*}
Q &= \frac{M_w}{M_n} = \frac{DP_w}{DP_n} = \frac{\mu_2}{\mu_0} \frac{\mu_0}{(\mu_1)^2} \quad (6.1) \\
\sigma_n^2 &= \frac{\mu_2}{\mu_0} - \left(\frac{\mu_1}{\mu_0}\right)^2 \quad (6.2) \\
\theta &= M_w - M_n = m \sigma_n^2 \left(\frac{\mu_1}{\mu_0}\right) \quad (6.3) \\
\Delta &= \sqrt{Q - 1} = \frac{\sigma_n}{DP_n} \quad (6.4)
\end{align*}

Variance and Polydispersity are related by,

\[ Q = 1 + \frac{\sigma_n^2}{DP_n^2} \quad (6.5) \]

Where $m = \text{polymer molecular mass}$ and other terms as described as above.
Chapter 6: Simulation Results

Their graphical profiles relating to various bond scission rates and moment parameters with respect to either decreasing DPn or progress in decay time are given in figures 6.1d to 6.10h. The graphical presentations of the scission percent and rate characteristics between time cycles are given in Fig6.1d-6.10d. Total bond mobilisation per cycle per hour, compared to the initial starting point, is given in Fig. 6.1e-6.10e. The graphs showing the variation of Polydispersity (Q) and Delta (Δ) are presented in 6.1f-6.10f and the variation of Theta (θ) and Variance (σ) with the fall of DP are presented in 6.1g-6.10g. The fall of Mn over decay time is shown in Fig. 6.1h-6.10h. These simulation results are described briefly next.

Let's first consider the kinetics of bond mobilisation between time cycles i.e. the Scission percent and rates per hour profiles (Fig. 6.1d-6.10d) and over all mobilisations compared to the initial time i.e. total Turnover reaction (Fig. 6.1e-6.10e). In most cases, two consecutive peaks were observed (except in trend 8) in the Scission percent profiles. A smaller peak occurred at the early phase around 1500 hrs reaching between 25-55%, followed by another at the late phase around 9000 hrs, reaching approximately 45-60%. In between these two extremes, the amount of bond scission in consecutive cycles tended to remain steady at 41-45% (depending on different trend individual profile). The reactions tended to level up by 11,000 hrs.

Scission hourly rates varied with time as above but with a prominent peak trajectory by the end of early phase. In most cases, the highest rate occurred in between early to middle phase of decay around 1500 hrs. The maximum number of bond mobilisations varied among the trends, with a lowest of 45,000 and a highest of 155,000 per hour (212,000 for trend 8). The rate then dropped abruptly reaching a minimum by 4500 hrs and started to level up between 8500-9000 hrs with little fluctuation and finally reached a plateau by 11,000hrs. The small variation between the cycles is caused by variation in the amount and percent of unzipping reaction. Number of bond
Fig. 6.1d-6.4d: Intermediate Scission Comparison Between Cycles for Trends 1-4
Fig. 6.1-6.4: Estimate of Bond Mobilisation Per Cycle from the Initial Total for Trends 1-4
Fig. 6.5d-6.8d: Intermediate Scission Comparison Between Cycles for Trends 5-8
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Table 6.5-6.8c: Estimate of Bond Mobilisation Per Cycle from the Initial Total for Trends 5-8

<table>
<thead>
<tr>
<th>Trend</th>
<th>Initial Total (per cycle)</th>
<th>Per Cycle</th>
<th>Per Minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.75</td>
<td>0.01</td>
<td>0.004</td>
</tr>
<tr>
<td>6</td>
<td>0.80</td>
<td>0.02</td>
<td>0.008</td>
</tr>
<tr>
<td>7</td>
<td>0.85</td>
<td>0.03</td>
<td>0.012</td>
</tr>
<tr>
<td>8</td>
<td>0.90</td>
<td>0.04</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Graphs showing trends in bond mobilisation per cycle from the initial total for Trends 5-8.
Fig 6.9 d-6.10d: Scission and Fig 6.9e-6.10e: Turnover graphs for Trends 9 and 10
mobilisation is accelerated via Unzip or Cutchop action per cycle by the end of midphase changing the shapes of the scission percent graph. The trend graphs for total bond turnover percent and rate (per cycle per hour) compared to the initial i.e. zero time total (Fig. 6.1e-6.10e) display similar patterns. The rate graph gave a single peak at approximately 1500 hrs. (i.e. between early-mid phase) where the maximum amount of mobilised bonds was 45,000-65,000 per hour (88,000 for trend 7). The peak then started to fall and reached a minimum by 7000-8000 hrs when it levelled up. The percent graph, on the other hand, displayed a gradual smooth rise, reaching a maximum by 9000-10,000 hrs when 84-95% scission had been performed. The smooth rise and fall of both curves with gradual slopes and end plateaux arise because the total turnover reactions are related to the total number of intact bonds available at the onset of each decay cycle, which decreases smoothly in the simulations.

The simulated number average molecular weight (Mn) vs. time graphs for trends 1-10 are given is Fig. 6.1h-6.10h. These show a perfect exponential decrease in Mn with degradation. Each trend (except trend 2) reflected a smooth curve with sharpest descent at the early time between 0hr-4000hrs approximately, followed by a slow down and levelling out in rate by 8000hrs. The slope of the early decrease may differ slightly from one trend to the other, depending on the ratio of percent occurrences of end cut scission events (e.g. Cutlength, Cutpercent or Cut-in-half) to those of unzipping (e.g. Unzip or Cutchop). For example trend 9 and 1 show sharper slopes than trends 3 and 8. The best result is presented by trend 10 which showed the closest early slope to the lab-test data (DPn Vs time curve). Curve bulging in some of the graphs is due to the smoothing routine.

The graphical relation of DPn decrease, as an indication of progress of decay, with Polydispersity (Q) and Delta (Δ) (Fig. 6.1f-6.10f) show a negative co-linearity. The large increase of Q in trends 3, 4, 7, 8 and 9 is due to high end-cut scissions and low unzipping. High numbers of the smaller fractions together with low numbers of the longer molecules give low
Chapter 6: Simulation Results

second moment values, which control the extent of diversity of the magnitudes Q and Δ. Q and Δ rose slowly (keeping between 1-3) as DPn fell to 1/3rd of its initial value, after which the index rose faster, indicating severe invasion in the longest chain i.e. the crystalline regions, with the loss of physical order in the polymer substrate. The rise in more advanced decay phases was more prominent in Q than Δ since the latter reflects a fraction of this dispersion about the mean. Unzip reduces the breadth of Q by its annihilation effect, as observed in Trend 1.

Figures 6.1g-6.10g show the effect on other quantities, such as σ and θ, which measure the depth of decay reaction in the stable domains of the polymer. The graphs show steady slow decreases in both with decreasing DPn through the entire decay, revealing a positive co-linearity between the three parameters. Decrease in θ indicates decrease in weight average degree of polymerisation compared to number average. This in turn indicates a gradual loss of the long chain species and steady accumulation of the short chain species. The first quarter of the Mn vs. time curves (Figures 6.1h-6.10h) revealed an approximate steady linear decrease in Mn indicative of a 1st order relationship in the early decay phase. The steady kinetics then changed abruptly towards a non-linear relationship as the number of high molecular weight chains was reduced by percent cut or end chopping mechanisms. This also indicated that bond scission invasion occurred primarily in the crystalline or semi-crystalline regions. Unzipping mechanisms continued to eliminate most of the new generations of smaller fractions from the reactor, otherwise accumulation of low molecular weight fraction would have been observed in the MWD curves. This is also reflected in the θ and σ graphs and the Q and Δ relationships, which all show co-linearity with DPn changes without any abrupt changes during the early phase of decay.
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Fig. 6.1f-6.10f: Polydispersity and Delta Profile Vs DP (Trend 1-10)
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Fig. 6.1g-6.10g: Variance & Dispersion (Theta) Vs DP (Trends 1-10)
Fig. 6.1h-6.10h: Average Mn Change Vs Decay Progress (Trends 1-10)
6.4. Effects of Temperature

The following observations from simulation experiments (based on cellulose decay results from the accelerated lab-tests at three temperatures 120°C, 140°C and 160°C) reflect the accelerating effect of temperature on the rate of reaction.

6.4.1. MWD Profiles (Fig. 6.11 a-c – 6.13 a-c)

Figures 6.11 a-c – 6.13 a-c present simulated MWD curves obtained from (a) Slider, (b) Markov and (c) Algebraic exact Mathematical models for three temperatures 120°C, 140°C and 160°C respectively and show faster mobilisation of the longest chains and faster peak-shifts from HMW to LMW as the temperature increased. For example, the MWD curve peak shifts from its initial position at 6 (appx.) on the x-axis log-scale, at the onset of decay, to its limiting LMW position, in 596hrs at 160°C, 2432hrs at 140°C and 12,000 hrs (appx) at 120°C.

The other noticeable effects are more decrease in bimodality and initial peak broadening and increase in initial peak height loss with temperature rise. This may be due to the extent of unzip operation during the initial decay phase. Figures 6.23 a, b, e, f, l and j show the effects of different ratios of percent of unzip to end-cut scission mechanisms on Mn, Mw and Q respectively at low temperature (120°C) and Fig. 6.23 c, d, g, h, k and l at high temperature (160°C). The higher the ratios of unzip to end-cut scissions, the lower the molecular density dispersion (Q). The effects of full unzip as opposed to partial unzip on the decrease in Mn and Q seem to have opposite effects at lower and higher temperatures. However, the change in DP and Mw seem to remain the same irrespective of temperature increase. The effect of partial unzip (cut-chop scission mechanism) of the end-cut fragments is to increase the molecular size-breadth rather than inhibiting it as expected from a full unzip. This is most likely to occur in the lower temperatures due to insufficient supply of vibrational energy, which in
Fig. 6.11 a-c: MWD Profile for 120°C (a) Slider, (b) Markov (c) Maths
Fig. 6.12 a-c: MWD profile for 140°C (a) Slider, (b) Markov, (c) Maths
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Fig. 6.13 a-c: MWD profile for 160°C (a) Slider, (b) Markov, (c) Maths
turn suppresses the mobility or spread of radical reactions. There are indications in the literature of change in the reaction mechanisms at lower temperatures (Razumova et al., 1987; Saito et al., 1957; Hino and Suganuma, 1967, 1972; Croce and Camozzi, 1984, Emsley and Stevens, 1994b).

6.4.2. Moment Profiles (Fig. 6.14a-6.16f)

Examples of $DP_n$ changes over time for each of three temperatures are cited in Fig. 6.5-6.7 a-c for the three models (a) Slider, (b) Markov and (c) Exact Maths. Each show the same exponential fall in the very early decay phase followed by an end plateau at the limiting DP (150-200 appx.). The slopes of this initial rapid fall differ from model to model with the steepest slopes obtained from Markov model. The equivalent changes in $DP_w$ and $M_n$ exhibit the same trends, as seen in figures 6.5d-h (120°C), 6.6c-f (140°C) and 6.7c-f (160°C).

6.4.3. Bond Scission Percent and Rate Profiles (Fig. 6.17a-6.19f)

Figures 6.17a-c, 6.18a-c and 6.19a-c show the instantaneous rate of bond scission (pink dots) and the percentage of bonds breaking as a fraction of the original number (green dots) between time segments (i.e. cycles) /sec, /min and /hour at 120°C, 140°C and 160°C. Similarly, figures 6.17d-f, 6.18d-f and 6.19d-f show the equivalent total percentage and absolute rates of scission. The three rate-graphs (/sec, /min and /hour) show apparent fluctuations due to the overall random nature of disintegration in Slider iteration and exhibits more detailed information with respect to all three rates. This is more apparent in the amount of bond scission between cycles than when compared to the initial total. A uniform consistency is preserved among the three rates and the percent profiles for all three temperatures, except for a small difference between the second and hour rate profile observed at 140°C. The variability may or may not be significant, but is not
Simulation of Cellulose Ageing in Oil at 120°C

Fig. 6.14 a-c: DPn drop over time (a) Slider, (b) Markov, (c) Maths
Simulation of Cellulose Ageing in Oil at 120°C

Fig. 6.14 d-g: DPw (d) Slider, (e) Markov Models and Mn (f) Slider, (g) Markov Models Vs time
Simulation of Cellulose Aging in Oil at 140°C

Fig. 6.15 a-c: DPn (a) Slider (b) Markov; DPw (c) Slider Vs time

![Graphs showing DPn and DPw over degradation time for different methods.](image-url)
Simulation of Cellulose Aging in Oil at 140°C

Fig. 6.15 d-f: DPw (d) Markov; Mn (e) Slider, (f) Markov Vs time
Simulation of Cellulose Aging in Oil at 160°C

Fig. 6.16 a-c: DPn (a) Slider (b) Markov; DPw (c) Slider Vs time
Simulation of Cellulose Aging in Oil at 160°C

Fig. 6.16 d-f: DPw (d) Markov; Mn (e) Slider, (f) Markov Vs time
uncommon in reality due to temperature influence on reactions and intervals. To minimise the number of graphs displayed only those from the Slider model are included.

The highest rates of bond mobilisation (175,000/hour/cycle at 160°C) result in almost 99% conversion achieved within 200 hours, after which the rate drops to a plateau after about 900 hours. Only 57% conversion is achieved at 140°C after approx. 600 hours and the same is achieved at 120°C after 2000 hours. Highest scission rates occur in the early cycles when maximum bonds are available. The simulated bond scission rate curves show scission rates 20 times faster at 160°C (190,000/hour after 40-50 hours) than at 120°C (130,000 after 800-900 hours). The maximum total scission rate at 120°C occurs at 900-1000 hours and about 30% total percentage bond scission, which increases to a maximum of 70% by 8000 hours before levelling off. This plateau point is reached by 1731 hours (i.e. almost 5 times faster) at 140°C and by 200 hours (i.e. almost 40 times faster) at 160°C.

The percentage of total conversion at 140°C does not show the same peak maximum as seen at 120°C and 160°C. The scission graphs indicate that partial scission of the longest chains (possibly corresponding to the crystalline regions) occurs in the early stages at 120°C and remains incomplete into the end phase. Scission continues well into the mid phase of decay at 140°C and is complete within a few hours at 160°C. As a result, DP decrease at 120°C levels off between 400-500 and never reach the critical 200 values where the polymer loses all mechanical strength (Emsley et. al, 2000b).
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Simulation of Cellulose Ageing in Oil at 120°C

Fig 6.17 a-c: bond scission profile between time cycles per
(a) Second (b) Minute and (c) Hour

---

Intermediate Reaction (No. Bond-Scission) Percent/Rate Compared to Previous Cycle

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172a
Simulation of Cellulose Ageing in Oil at 120°C

Fig 6.17 d-f: total bond scission profile from decay-start per (d) Second (e) Minute and (f) Hour
**Simulation of Cellulose Ageing in Oil at 140°C**

Fig 6.18 a-c: bond scission profile between time cycles per
(a) Second (b) Minute and (c) Hour

<table>
<thead>
<tr>
<th>Time Unit</th>
<th>Reaction Rate Compared to Previous Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-577 sec</td>
<td>0-1154 sec</td>
</tr>
<tr>
<td><strong>Sec</strong></td>
<td><strong>Min</strong></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14.29</td>
<td>85.71</td>
</tr>
<tr>
<td>34.90</td>
<td>28.57</td>
</tr>
<tr>
<td>67.14</td>
<td>42.06</td>
</tr>
<tr>
<td>90.71</td>
<td>57.14</td>
</tr>
<tr>
<td>114.36</td>
<td>71.43</td>
</tr>
<tr>
<td>138.01</td>
<td>85.71</td>
</tr>
<tr>
<td>161.66</td>
<td>100</td>
</tr>
</tbody>
</table>

**Degradation Time (Hours)**
- Per Hour/Per PDCycle
- Per Minute/Per PDCycle
- Per Second/Per PDCycle
Simulation of Cellulose Ageing in Oil at 140°C

Fig 6.18 d-f: total bond scission profile from decay-start per (d) Second (e) Minute and (f) Hour

![Graph showing total reaction turnover percent/hour compared to initial concentration for different time intervals.](image)
Simulation of Cellulose Ageing in Oil at 160°C

Fig 6.19 a-c: bond scission profile between time cycles per
(a) Second (b) Minute and (c) Hour

Intermediate Reaction (No. Bond-Scission) Percent/Rate Compared to Previous Cycle

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Percent/Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>75.71</td>
</tr>
<tr>
<td>400</td>
<td>57.14</td>
</tr>
<tr>
<td>600</td>
<td>42.96</td>
</tr>
<tr>
<td>800</td>
<td>28.57</td>
</tr>
</tbody>
</table>

172e
Simulation of Cellulose Ageing in Oil at 160°C

Fig 6.19 d-f: total bond scission profile from decay-start per (d) Second (e) Minute and (f) Hour
6.4.4. Molecular Density Dispersion Profiles
(Fig. 6.20 a-d - 6.22 a-d)

Polydispersity Q and its various statistical measures such as $\Delta$, $\theta$, and $\sigma$ are plotted against the fall in DP in Fig 6.11a-d for 120°C, Fig. 6.12a-d for 140°C and in Fig. 6.13a-d for 160°C for the two models - Slider and Markov. Both models show a slow increase in Q and $\Delta$ with decreasing DP until the latter falls to 1/3rd to 1/2 of its initial value, and display negative co linearity throughout. Both then rise towards the end of reaction, with the rise being most prominent at 160°C and 1/2 the initial DP. The $\theta$ and $\sigma$ both decrease towards the end of reaction, which reflects the gradual accumulation of chain fragments of variable sizes as reaction proceeds.

6.4.5. Effects of Scission Ratios On Moments
(Fig. 6.23 a-l)

At 120°C, weaklink and cutlength scission mechanisms increase in the advanced decay phase, which produces a wide range of fragment sizes, unless these lower molecular weight fragments are dissipated by means of full unzipping, as shown in fig. 6.14 a and b, i, j. The lower the percentage (<20%) of end-cut, the less the fall in Mn and Mw. Increasing the temperature (e.g. to 160°C) increased the percentage of endchop and unzip as indicated by fig. 6.14 c, d and k, l.

These graphs also provide an estimation of the probability of the lab-test acquired Mn falls between 42% and 45% end-cut margin compared to the simulated samples at lower temperatures (e.g. 120°C). At higher temperatures (e.g. 160°C), when cut-percent and full unzip mechanisms are more predominant, as indicated by simulation experiments, the lab-test Mn comes close to a zip-ratio index of 0.25 from the start of decay until DP falls to below 1000. Following the latter, lab-test Mn fall increases and approaches a zip-ratio index between 0.63 and 0.65 until DP falls below half of its original size, when this further increases to an index between 0.73 and
Simulation of Cellulose Aging in Oil at 120°C

Fig 6.20a-d: polydispersity-delta vs. DP fall (a) Slider (b) Markov; variance-theta vs. DP fall (c) Slider (d) Markov
Simulation of Cellulose Aging in Oil at 140°C

Fig 6.21a-d: polydispersity-delta vs. DP fall (a) Slider (b) Markov; variance-theta vs. DP fall (c) Slider (d) Markov
Simulation of Cellulose Aging in Oil at 160°C

Fig 6.22a-d: polydispersity-delta vs. DP fall (a) Slider (b) Markov; variance-theta vs. DP fall (c) Slider (d) Markov
0.77 in the more advanced phase (see figures 6.23c and d). The falling
trend of Mw of the labtest resembles that of a sample zip-ratio index
between 0.55 and 0.65 during the early state of decay to the mid phase
(indicated by DP fall to half its original size) and thereafter between 0.63 and
0.65 (Fig. 6.23 k and l).

Fig. 6.23e shows the opposite effect of cut-chop (with partial unzip), where
the drop in Mn is less at higher percent chop than at low. Fig. 6.23f shows
that increasing the %endcut increased the rate of DP fall. Figures 6.23g and
6.23h show full unzip inhibited MWD curve spreading at both low and high
temperatures. The temporal changes from the main scission mechanisms as
discussed above is summarise in the following table.

<table>
<thead>
<tr>
<th>Decay Phase</th>
<th>%endcut</th>
<th>%unzip</th>
<th>%cutchop</th>
<th>zipratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>20</td>
<td>10</td>
<td>75</td>
<td>0.77</td>
</tr>
<tr>
<td>140°C</td>
<td>30-35</td>
<td>40</td>
<td>20-25</td>
<td>0.36</td>
</tr>
<tr>
<td>160°C</td>
<td>25</td>
<td>65</td>
<td>10</td>
<td>0.45</td>
</tr>
<tr>
<td>Mid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>45-48</td>
<td>12</td>
<td>42</td>
<td>0.95</td>
</tr>
<tr>
<td>140°C</td>
<td>20</td>
<td>45-50</td>
<td>5-10</td>
<td>0.55</td>
</tr>
<tr>
<td>160°C</td>
<td>20</td>
<td>67</td>
<td>5</td>
<td>0.73</td>
</tr>
<tr>
<td>Late</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>26</td>
<td>15</td>
<td>20</td>
<td>0.55</td>
</tr>
<tr>
<td>140°C</td>
<td>25</td>
<td>45-50</td>
<td>5-8</td>
<td>0.65-0.67</td>
</tr>
<tr>
<td>160°C</td>
<td>25</td>
<td>72</td>
<td>2</td>
<td>0.73-0.77</td>
</tr>
</tbody>
</table>

Table 6.19: Simulation experiment predicted estimation of extents of
main scission mechanisms and zip-ratios with variable temperatures
and gradation of decay phases.
Effect of Scission Events on Mn of Simulated Samples compared to Lab-test with the rise in Temperature in Oil (120\(^0\)C-160\(^0\)C)

Fig. 6.23 a-d: the effect of unzip on Mn Vs Time. (a) 120\(^0\)C, (c) 160\(^0\)C and on Mn Vs DP fall (b) 120\(^0\)C, (d) 160\(^0\)C
Effects of Scission Events on DP and $Q$ of Simulated Samples compared to Lab-test with the rise in Temperature in Oil ($120^\circ$-$160^\circ$C)

Fig. 6.23 e-h: effects of (e) % cutchop on Mn, (f) % endcut on DP, % unzip on $Q$ - (g) $120^\circ$C, (h) $160^\circ$C
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Effect of Scission Events on Mw of Simulated Samples compared to Lab-test with the rise in Temperature in Oil (120°C-160°C)

Fig. 6.23 i-l: effects of zlip-ratios on Mw Vs Time, (i) 120°C, (k) 160°C and on Mw Vs DP fall (j) 120°C, (l) 160°C.
6.5. Effects of Environment

6.5.1. Simulation of Synergistic Effects of Heat and Moisture with Oxygen Antagonism (Fig. 6.24 a-d)

Experimental observations on the decay patterns of cellulose substrates in oil under temperature, moisture and oxygen conditions have indicated the possibility of antagonistic interactions between water and oxygen at low water and temperature levels (Emsley et al., 2000a). In comparison, the interactions between water and temperature are strongly synergistic and between oxygen and temperature more weakly so. These environmental conditions are simulated using the following event strategies.

(a) The effect of thermohydrolysis – a combination of Cutpercent and Cutchop mechanisms.

(b) The effect of oxygen antagonism – reaction interfering factors.

(c) The effect of thermal acceleration – by increasing the percent of Unzipping mechanisms.

The simulation results are given in Fig. 6.24 a-d, where the top two graphs (Fig. 6.24a-b) show how different proportions of H$_2$O: O$_2$ affect DP fall and the bottom two graphs (Fig. 6.24c-d) show their effect on the Q parameter at the two temperatures 120°C and 140°C. The top two graphs clearly show much slower DP fall in the low water level conditions in comparison with the high water levels at both temperatures. Similarly the bottom two graphs display significant rate increases in the index of Q in high water level conditions, but inhibited rates in the low or medium water level conditions. This indicates less vigorous reactions in the latter, resulting in a lower yield of chopped fragments, which inhibited the DP fall and increased Q. However, irrespective of the presence of oxygen (i.e. high/low/medium), the invasion by both thermal and hydrolytic scission mechanisms continued.
Simulation of Environmental Effects on Ageing of Cotton Linters in Oil

(effect of water-Cutchop+Cutpercent, effect of $O_2$, other interferences, effect of thermal acceleration – Unzip)

Fig. 6.24 a-d
unhindered by oxygen antagonism. The differences in DP fall and Q increase seemed to be a little more pronounced at 140°C than at 120°C. This may be due to more dominant thermolytic unzipping mechanisms at the higher temperature, which inhibited increase in size-breadth by removing oligomer fractions. Thermally induced reactions are found to be the major degradative factors to cause the loss of mechanical strength of paper insulation (Emsley and Stevens, 1994a, b, Darveniza et al., 1992, 1993).

6.5.2. Simulation of Differential Rates of Subsets in Air and Oil (Fig. 6.25 a-f and Tables 6.20 and 6.21)

A comparative study of the simulated reactivity rates of the 6 subsets of polymer (cellulose substrates) in oil and air is portrayed in Figures 6.16 a-f. The variations of simulated probable reaction rates were studied for all three temperatures - 120°C profile presented in Fig 6.25a (air) and b (oil), 140°C in Fig 6.25c (air) and d (oil) and finally 160°C in Fig 6.25e (air) and f (oil) respectively. These results show the differences in rates in air and oil and help to define the nature of breakdown in the different structural domains and why polymer-ageing kinetics are so complex. The use of simulation experiments makes it possible to further breakdown the kinetic rate into that for each individual molecular subset, treating each one as a separate component of the macro-structure. The reaction pathways of these individual components vary enormously as reflected in these graphical representations and are impossible to obtain from practical experiments. For example, subsets 1 and 2, which might symbolise the smallest chains residing in the amorphous or the least ordered domains of the polymer matrix, display the lowest reactivity of the order of 2% - 10%. The highest MW subsets (symbolised by subsets 5 and 6) show the most significant thermal susceptibility at between 20% and 45%. The molecular species in between these two extreme arrays are the medium sized chains (symbolised by subset 3 and 4), which might be located in the semi-ordered domains and they display a constant reactivity of around 15%-25% throughout the different advanced phases of decay. The most significant
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%Probability Rate Graphs of Molecular Subsets at 120°C

Fig. 6.25a: Air and Fig. 6.25b: Oil

%Probability Weights of Reactivity Variations among Polymer Subsets Over
Decay Time (hrs) at 120°C in Air

%Probability of Reaction Rate Variations among the Polymer Subsets
Over Decay Time (hrs) at 120°C in Oil
Chapter 6: Simulation Results

%Probability Rate Graphs of Molecular Subsets at 140°C

Fig. 6.25c: Air and Fig. 6.25d: Oil

%Probability Weights of Reactivity Variations among Polymer Subsets
Over Decay Time (hrs) at 140°C in Air

%Probability of Reaction Rate Variations among the Polymer Subsets.
Over Decay Time (hrs) at 140°C in Oil

176b
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%Probability Rate Graphs of Molecular Subsets at 160°C

Fig. 6.25e: Air and 6.25f: Oil

%Probability Weights of Reactivity Variations among Polymer Subsets
Over Decay Time (hrs) at 160°C in Air

%Probability of Reaction Rate Variations among the Polymer Subsets
Over Decay Time (hrs) at 160°C in Oil
**Probability Tables of Simulated Rate Variations of Polymer Subsets in Air and Oil**

### Table 6.20: Air

<table>
<thead>
<tr>
<th>Decay Phase</th>
<th>Low MW Subsets</th>
<th>Medium MW Subsets</th>
<th>High MW Subsets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>17%</td>
<td>43%</td>
<td>40%</td>
</tr>
<tr>
<td>140°C</td>
<td>23%</td>
<td>38%</td>
<td>38%</td>
</tr>
<tr>
<td>160°C</td>
<td>25%</td>
<td>42%</td>
<td>33%</td>
</tr>
<tr>
<td>Mid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>20%</td>
<td>44%</td>
<td>36%</td>
</tr>
<tr>
<td>140°C</td>
<td>18%</td>
<td>36%</td>
<td>46%</td>
</tr>
<tr>
<td>160°C</td>
<td>12%</td>
<td>47.5%</td>
<td>41%</td>
</tr>
<tr>
<td>Late</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>26%</td>
<td>40%</td>
<td>36%</td>
</tr>
<tr>
<td>140°C</td>
<td>24%</td>
<td>50%</td>
<td>26%</td>
</tr>
<tr>
<td>160°C</td>
<td>14%</td>
<td>27%</td>
<td>60%</td>
</tr>
</tbody>
</table>

### Table 6.21: Oil

<table>
<thead>
<tr>
<th>Decay Phase</th>
<th>Low MW Subsets</th>
<th>Medium MW Subsets</th>
<th>High MW Subsets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>18%</td>
<td>24%</td>
<td>50%</td>
</tr>
<tr>
<td>140°C</td>
<td>21.3%</td>
<td>32%</td>
<td>46.81%</td>
</tr>
<tr>
<td>160°C</td>
<td>20.58%</td>
<td>35.29%</td>
<td>44.12%</td>
</tr>
<tr>
<td>Mid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>17.5%</td>
<td>31.25%</td>
<td>51.25%</td>
</tr>
<tr>
<td>140°C</td>
<td>18.19%</td>
<td>36.36%</td>
<td>45.45%</td>
</tr>
<tr>
<td>160°C</td>
<td>25.42%</td>
<td>38.98%</td>
<td>35.59%</td>
</tr>
<tr>
<td>Late</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>21.57%</td>
<td>47.06%</td>
<td>31.37%</td>
</tr>
<tr>
<td>140°C</td>
<td>22.5%</td>
<td>27.5%</td>
<td>50%</td>
</tr>
<tr>
<td>160°C</td>
<td>20%</td>
<td>42%</td>
<td>30%</td>
</tr>
</tbody>
</table>
invasion in the HMW regions is achieved at the highest temperature (i.e. 160°C), and is more clearly exhibited in oil than in air. Semi-crystalline regions (subsets 3 and 4) seemed to be most affected at 140°C in both oil and air. The invasion of ordered or semi-ordered (i.e. HMW and MMW) regions was less profound at 120°C and rapidly tailed off, showing that thermal and hydrolytic reactions are not strong enough to persist into the late phase of decay. The lower middle chains are most affected at this temperature.

The effects observed can be summarised as follows:

- subset 1 displayed the least reactivity in both air and oil
- subset 2 more was reactive in air than in oil reaching its highest value during the early mid-phase at 160°C and late phase at 140°C.
- subset 3 was most reactive at low temperatures in air, reaching 30% activity
- subset 4 is more reactive than subset 3 at all 3 temperatures and more so in air than oil.
- subsets 5 and 6 are much less reactive in air than in oil, reaching 23-25% in the former compared to 40% in the latter.

These effects might be interpreted as follows:

- thermal and thermo-hydrolytic effects are much stronger than thermo-oxidative effects in oil due to interfering proton abstraction by oxygen.
- thermal and auto-radical reactions, probably unique to air are much stronger than the above.
- invasion of the HMW regions requires high thermal input - around 160°C or above, while Medium MW regions or semi-crystalline regions become susceptible at medium temperatures in both air and oil.

The above analysis in brief, indicates air is more destructive than oil, which is in turn should be ideally more destructive than vacuum. The rates for each of low, medium and high molecular weight subsets are given for both air and oil graded by early, mid and late decay phases in the tables in Tables 6.3 and 6.4 respectively.
6.5.3. Environmental Effects On MWD Peak-shifts
(Fig. 6.26 a-d, Fig. 6.27 a-e, Fig. 6.28 a-e)

An alternative way to estimate decay progress in terms of both time and
temperature could be in terms of measuring the time of MWD curve-peak
shifts from HMW region toward LMW region. We can then use an empirical
relationship, such as equation 6.6, to extrapolate to lower temperatures.

\[ \Delta t = C \pm 2a \left( \frac{\Delta T}{b} \right)^x \]  

Where
\( \Delta t \) = time increase/decrease for a temperature decrease/increase of \( \Delta T \)
\( x \)=exponent (1,2,3,...) depending on the degree of lowering in temperature
\( b \)=constant depends on thermal sensitivity of the system
\( a \)=co-efficient that depends on the amount of kinetic rate change due to
increase in thermal energy and is related to the time elapsed between two
total peakshifts at the highest temperature (in this case 160°C). The time
difference can be further adjusted via the addition of or deduction of an
arbitrary quantity C, depending on whether the temperature is decreased or
increased.

Fig. 6.26a and b display the graphical relationship between the time
(years/hours) and total peakshifts and show the effects of temperature,
based on the above equation and accelerated labtest results (both air and
oil), extrapolated to lower temperatures. The effects of slower rates of decay
in an electrical transformer environment are also shown for both air (Fig.
6.26c) and oil (Fig. 6.26d). The graphs also show how much shorter the
timescales are in air than in oil. This is reinforced in separate time-
temperature graph for each of 5 individual peaks for air (Fig. 6.27a-e) and
for oil (Fig. 6.28a-e) and show that time and temperature effects can be
represented by a polynomial function relationship.
**Peak-shift Time (Hours, Years) Vs Temperature Plot Showing Slow and Accelerated Decay of Cotton Linters in Air and Oil**

Fig. 6.26 a-d: Accelerated decay (a) air, (b) oil and Slow decay (c) air, (d) oil
**Individual Peak-shift Time (hrs) Vs Temperature (°C) in Air**

Fig. 6.27a-d

**Time (hrs) for Peakshift (6-5.8) Vs Temperatures (°C) in Air**

- **Graph a:**
  - Temperature (°C) vs. Time (hrs)
  - Peakshift (5.8-6)

- **Graph b:**
  - Temperature (°C) vs. Time (hrs)
  - Peakshift (5.8-5.4)

- **Graph c:**
  - Temperature (°C) vs. Time (hrs)
  - Peakshift (5.4-5.8)

- **Graph d:**
  - Temperature (°C) vs. Time (hrs)
  - Peakshift (5.4-5.8)
Fig. 6.28a-d

Individual Peak-shift Time (hrs) Vs Temperature ($^\circ$C) in Oil

- **Fig. 6.28a**: Graph showing peak shift time vs temperature for a specific case.
- **Fig. 6.28b**: Similar graph for another case.
- **Fig. 6.28c**: Graph with data for a different scenario.
- **Fig. 6.28d**: Graph depicting yet another case.

These figures illustrate how peak shift time varies with temperature in different conditions.
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**Individual Peak-shift Time (hrs) Vs Temperature (°C)**

**Fig. 6.27e:** Peak-shift 5 in Air; **Fig. 6.28e:** Peak-shift 5 in Oil

---

**Time (hrs) for Peakshift (4.8-4.6) Vs Temperatures (°C) in Air.**

---

**Peakshift (4.8-4.6) Time(hrs) Vs Temperatures (°C) in Oil**

---

178d
6.5.4. Environmental Effects on Decay Rates
(Fig. 6.29 a-g)

Degradation rates are calculated for each time cycles on the basis of experimental labtest data and the kinetic rate time model 1 (Emsley and Heywood, 2000) and further extrapolated to lower temperatures by using equation 6.6, above. Fig. 6.29 a-d shows an exponential rise in the decay rate in air after 120°C and after 100°C in oil (Fig. 6.29 e-g). It is more pronounced in cycles 2, 5 and 7 in air and in cycle 2 and 4 in oil. The least increase is shown by cycles 6 and 7 in air and cycle 7 in oil, which showed a linear increase with a very low slope. This may explain the early rapid fall in cellulose DP as the degradation rates rise exponentially, followed by a sudden slow down as the rate approaching the limiting DP of 200.

6.5.5. Environmental Effects on Estimation of Polymer Durability (Fig. 6.30 and 6.31 a-b)

The estimated (described in 6.5.3) peakshift times plotted against DP show the early exponential curve becoming relatively flatter at temperatures of 140°C and below. Figures 6.30 a-b shows slow decay of cotton linter in air and 6.31 a-b the same in oil over a range of temperatures (60°C-160°C). The individual curves are inset on expanded scales for better clarity. The sharp fall in DP in both air (Fig. 6.30a) and oil (Fig. 6.31a) at 160°C begins to show a small degree of flattening at 120°C, which becomes more pronounced at 100°C – 40°C, in both air (Fig. 6.30b) and oil (Fig. 6.31b). Flattening is relatively greater in oil than air, due to the higher rate of decomposition in air than in oil.

In summary, the lower the temperature the less the degree of thermal input and hence the more retarded the rate of decomposition and the flatter the rate curves at long times. In reality, they can be expected to gradually drift from exponential to linear with a very low slope as the temperatures decreases.
Effect of Temperature (°C) on Simulated Degradation Rates in Air

Fig. 6.29 a-d: degradation-cycle/s (a) 1, (b) 3, 4, 5, (c) 2 and (d) 6, 7, 8
Effect of Temperature (°C) on Simulated Degradation Rates in Oil

Fig. 6.29 e-g: degradation-cycle/s (a) 1, (b) 4 and (c) 2, 3, 5, 6, 7, 8
Chapter 6: Simulation Results

Prediction of Durability of Cotton Linters at 120°C, 140°C, 160°C in Air

Fig. 6.30a

Rise in Peakshift Time (Years) with Temperature Decrease and Fall in DP

- Peakshift Time (Years, 160°C)
- Peakshift Time (Years, 140°C)
- Peakshift Time (Years, 120°C)
Chapter 6: Simulation Results

**Prediction of Durability of Cotton Linters at 100°C, 80°C, 60°C and 40°C in Air**

*Fig. 6.30b*

**Rise in Peakshift Time (Years) with Temperature Decrease and Fall in DP**

- Peakshift Time (Years, 100°C)
- Peakshift Time (Years, 80°C)
- Peakshift Time (Years, 60°C)
- Peakshift Time (Years, 40°C)

---

**Time (Years)**

0 100 200 300 400 500 600 700 800

---

**Fall in DP**

0 200 400 600 800 1000 1200

---
Prediction of Durability of Cotton Linters at 120°C, 140°C, 160°C in Oil

Fig 6.31a

Rise in Peakshift Time (Years) with Temperature Decrease and Fall in DP

- Peakshift Time (Years, 160°C)
- Peakshift Time (Years, 140°C)
- Peakshift Time (Years, 120°C)
Prediction of Durability of Cotton Linters at 100°C, 80°C, 60°C, and 40°C in Oil

Fig. 6.31b

Rise in Peakshift Time (Years) with Temperature Decrease and Fall in DP

- Peakshift Time (Years, 100°C)
- Peakshift Time (Years, 80°C)
- Peakshift Time (Years, 60°C)
- Peakshift Time (Years, 40°C)
Such changes would be difficult to examine at low temperatures in a real laboratory based experiment, because the time scales would be so long. The above table (Table 6.22), constructed using equation 6.6, presents estimated functionable life of cellulose, for a wide range of temperature (40°C -160°C) in both air and oil. This assumed the usefulness of this polymer is industrially acceptable until its initial DP falls to 150-200.

The above figures agree well with the life prediction estimates of Emsley and Heywood (2000) using their kinetic equation (time model 1, see Chapter 5), where they estimated cellulose life in a transformer could extend to at least 300 years in dry air and 700 years in dry oil at 60°C. However the above estimation would differ if the decay time distribution were different. This demonstrated that polymer structural integrity can be maintained over a limited but greater length of time, yet fluctuation in both temperature and medium can dramatically shorten the later. Since structure and mechanical properties are inter-related (Pachter et al., 1996) the added advantage of biopolymers inheriting much greater strength through their helical-reinforcing effect than synthetic extended-chain polymers (Lewis, 1997), may be lost at the loss of their structural harmony.
6.6. Conclusions

♦ Statistically tested results: (refer to table 6.7 and 6.8 and Appendix 6) summarise the following.

(a) Mechanism 1 (Cutlength+Weaklink+Unzip) relating fixed length end-cut mechanism, in concert with unzipping operations of the chain fragments, appears to be more commonplace for molecular disintegration in air than in oil. In contrast, mechanism 3 (Cutpercent+Weaklink+Unzip) appears to be more statistically appropriate in oil, where both unzip alone or in conjunction with cutchop cleavages may co-exist in synergism. The intermediate decayed MWD curve broadening effects were more pronounced in oil than in air from GPC chromatograms. The simulation results in this thesis shows that the main reason of the former is partial zipping effects, which is also supported by the moment profiles as described in this chapter's result sections.

(b) To summarise, the statistical results demonstrate that mechanism 3 is the most important scission mechanism throughout the cellulose decay process. Mechanisms 1 and/or 2 compete with 3 depending on the type of medium in which the degradation is carried out. The extent of this interference is not necessarily dependent on temperature. However the rise in the latter increases the rate of the reactions and the entropy of the system, which may contribute to favour either mechanism 1 or 2.

♦ Effects of molecular mechanisms: The results obtained from the simulation experiment study with the MWD trends, obtained from different combinations of scission events indicated the following.
Chapter 6: Simulation Results

(a) Bi/tri modality is displayed by the MWD intermediates during the initial phase of decay by a combination of two scission mechanisms – 'Cutpercent' or 'Cutlength' and 'Weaklink'.

(b) The initial peak-splits into bi/tri modal or shouldering effect disappear with the introduction of unzipping effects i.e. 'Cutchop' or 'Unzip' mechanisms.

(c) Tri-modality in trends 3 and 7 were identified to be a pronounced effect of 'Cut-in-Half' i.e. central scission. The effect of the latter alone (i.e. not in combination with other scission modes) emerged as a multi-modal pattern, shown in Chapter 3. In this Chapter the algorithm was set on log-linear scale, which also showed trimodal patterns rather than bimodal when in combination with mixed scission modes. This mechanism has been shown to be more common in polymer chain decay affected by mechanical or stress induced mechanisms.

(d) Inclusion of more scission events (>3) in a Slider event oriented reaction composition tends to display more uniform lateral MWD curve shifts similar to the trend observed in the case of random and equivalent exposure of different molecular assemblies along the polymer matrix.

(e) Absence of 'Unzip' reaction resulted in more curve deformity and irregular undefinable shapes.

(f) 'Cutpercent' scission reaction tended to give rise to peak broadening effects in the MWD intermediates. The former exhibited the effects of thermo hydrolysis.

(g) 'Cutlength' displayed similar effects or shouldering and as such can be identified with the effect of thermolysis or a part of auto-radical chain reactions, those more likely to occur as the temperature rises.

(h) Occurrence of more 'Unzip' in the reaction strategy tended to minimise uncontrollable accumulation in chain sizes with the evolving generations of fragment population by its annihilating effect. This helped to restore a balanced Gaussian unimodal form of the MWD curves during the end decay phase. By controlling the curve broadening, this mechanism also controls continual high increase in polydispersity.
Chapter 6: Simulation Results

- **Effects of temperature**: Experimentation with three temperatures (120°С, 140°С and 160°С) provided a good basis for comparative study. On the basis of simulation investigations of a complex macromolecular (cellulose) degradation the following inferences can be drawn.

(a) The lower the temperature the more the rise in weaker links prevails during the earlier decay, which are then superseded by ‘Cutpercent’ or ‘Cutchop’ mechanism during the midphase of decay advancement. These mechanisms display the effects of hydrolytic attack in the more ordered regions or crystalline domains of the polymer.

(b) In the case of polymers of uni-helical backbone composition (e.g. cellulose, chitosan) persistent attacks on the long chain ‘tie’ molecules, which run from the crystalline to semicrystalline regions initiate the onset of progressive decay. ‘tie’ chains link together these two regions and hence build a bridge between the two domains.

(c) In the case of multi-helix polymers (e.g. DNA and RNA duplex and multistranded polysaccharides) the onset of initial deterioration occurs at the weaker links (those which are less shielded by co-operative forces) from the opposite direction between the strands facing each other.

(d) In the case of branched chain or crosslinked polymers (e.g. polyethylene, polypropylene) initial attacks persist on the most preferred end sites of branching from the parent molecules.

(e) The above 3 strategies have been found more likely to be brought about by hydrolytic or thermo hydrolytic or enzymatic action in the case of condensation polymers.

(f) The higher the temperature the more predominant is the reaction of ‘Cutlength’ mechanism in conjunction with ‘Unzip’. Both successfully simulated a reaction strategy of thermolysis (or auto catalysis).

(g) Bond scission rates and percent profiles both for between cycles and compared with the initial bond total has shown consistent results with each other and among the three temperatures and three rates (i.e. per second, per minute, per hour). The effect of temperatures is to increase the rapidity of reaction rates and percent mobilisation by approximately 20 times with every 20°С rise.
(h) More fluctuation of rates between the time-cycles was visible compared to the smooth rise in total bond turnover from the start, which can be accounted for by the overall random nature of the Slider model. This is also the reason for slight inconsistency between the smallest (e.g. per min) unit time rate profiles and their largest counterpart (e.g. per hour). This is more significant at 140°C.

(i) This variation among the number of bond scission trends may be justified in terms of the differences in the direction, amount and speed of configurational disruption and changes experienced by the constituent molecular assemblies. Availability of thermal quanta and vibrational energy is responsible for these disruptions among the helical configuration in the solid-state polymers. Thus certain scission mechanisms with lower thermo-dynamical demand can be preferred to those with higher demand. The latter reaction strategies thus can gain more predominance with the rise of temperature. Thus for example a combination of 'Weaklink' and 'Cutpercent' has been found preferable at the lowest temperature (i.e. 120°C) whereas 'Cutlength' and 'Unzip' were found to take precedence at the highest temperature (i.e. 160°C). A competition between these two extreme strategies probably accounted for the deformities observed in 120°C.

+ Effects of environment: How varying the surrounding environment of the reactor can influence the nature and progression of decay was examined thoroughly by simulation experiment. The latter proved to be more powerful and easily amenable to carrying out exhaustive study than can be possible from lab based experiment. Simulation of environmental changes such as reaction media (e.g. air, oil and vacuum) and proportions of degradative catalysts (e.g. oxygen, moisture, temperature) was affected in the respective experiment by means of program interface driven function commands and the resultant graphical profiles were examined. Important inferences drawn are given below.
(a) The differences in reaction medium (air and oil) influence profoundly the individual reaction kinetics and hence rates among the different reactive structural components (subsets) of polymer.

(b) The most significant invasion in the HMW regions is achieved at the highest temperature (i.e. $160^\circ C$), and is more clearly exhibited in oil than in air.

(c) Semi-crystalline regions (subsets 3 and 4) seemed to be most affected at $140^\circ C$ in both oil and air.

(d) The invasion of ordered or semi-ordered (i.e. HMW and MMW) regions was less profound at $120^\circ C$ in oil than air and rapidly tailed off.

(e) The above showed that hydrolytic reactions are less likely to persist into the moderate advanced phase of decay in oil at lower than at higher temperatures and least so in air.

(f) In contrast oxidative or thermal auto-catalysis seemed to be more predominant in air than in oil and were also promoted by the rise in temperature in both mediums.

(g) The lower middle chain subsets are most affected by the decrease of temperature in contrast to the higher to middle chain subsets.

(h) Simulated DP and Q profiles were obtained from simulation MWD experimental samples, which reproduced the antagonism between water and oxygen at low water and temperature levels, a stronger synergism between water and temperature and weaker synergism between oxygen and temperature, which has been observed in lab experiments.

(i) An estimation of the extents of the main scission mechanisms obtained from the simulation experiments at different temperatures and different stages of decay are given in table1.

Estimation of polymer durability or life expectancy: a method has been deduced to estimate durability in terms of peakshifts as shown in section 6.5.3. The equation 6.6 provides a time-temperature relationship and an alternative way to estimate decay progress in terms of measuring the time of MWD curve-peak shifts from HMW region toward LMW region. This can be extrapolated to the desirable temperatures of the actual reactor e.g. in the
case of commercial use of cellulosic materials the reactor operating temperature can be as low as 60-80°C. For example to reach the limiting DP (200-150) the highest temperature (160°C) would take 0.07 years in air and 12 years in oil, whereas operating temperature (60°C) this would be 400 years in air and 716.4 in oil. The later is in good agreement with the prediction of Emsley and Heywood (2000). These estimations obtained from equation 6.6 for a range of temperature are given in table 6.22.
Chapter 7

Simulation of Real-Time and Kinetics

(Results)

7.1. Introduction

7.2. Modelling of Real Time

7.2.1. Exponential Distribution

7.2.2. Poisson Distribution

7.2.2.1. Time Cycles as Poisson Process

7.2.3. Use of Rectangular Hyperbolic Function

7.2.4. Random Geometric Distribution

7.2.5. Comparison of Time Rate Curves

7.3. Death Model

7.3.1. Mathematical interpretation

7.4. Processing of Kinetic Results

7.4.1. Important Kinetic Parameters

7.4.2. Implications of Entropy and DP of Cellulose

7.5. Kinetic Results from Simulation Experiment

7.4.1. Comparison to Observed Results

7.6. Conclusions
7.1. Introduction

This chapter presents concepts of modelling real time as mentioned in Chapter 5 and a brief description of how they were derived. The new model equations were fitted cellulose experimental data using non-linear or 1st order kinetic trends. Due to time restrictions, only the general concepts are presented here with some preliminary results. Examples of kinetic quantitative outcomes are presented (for cellulose) using time model 1 and data acquired from simulation experiments, which show the potential of the computer simulation in the area of polymer degradation. Full details of the time model (2-4) equations are included in Appendix 7 (included in CD). Only the important stages of equation development are cited here.

7.2. Modelling of Real Time (Fig. 7.1)

As stated previously, there is no direct way to convert or deduce real time directly in the case of computer simulated polymer degradation experiments. The time distribution can take different forms and shapes that can be governed by fragmentation process for individual molecular chain species. Time evolution thus constitutes an inherent outcome of the process (Fig. 7.1). The following four methods have been investigated for mathematical modelling of simulation time:

(a) Exponential distribution of simulated time (time model 1)
(b) Poisson distribution of simulated inner cycles (time model 2)
(c) Using a derivative of a rectangular hyperbolic function (time model 3)
(d) Random Geometric distribution (time model 4)

Details of deriving equations for time model a and b are included in Appendix 7.
Time Evolution Pattern Emerged as Inherent Outcome of Molecular Scission Processes

Fig. 7.1

or possibly this shape?

or even possibly:

Different Pattern for Time Distribution
Chapter 7: Simulation of Real-Time & Kinetics

7.2.1. Exponential Distribution of Simulated Time
(time model 1)

The following non-linear equation (Emsley and Heywood, 2000) was used

\[
\frac{1}{DP_t} - \frac{1}{DP_0} = \frac{k_1}{k_2} \left[ 1 - e^{k_2 \tau} \right] \tag{34}
\]

Where \(k_1\) = the initial bond-breaking rate, \(k_2\) = the rate constant at which \(k_1\) changes. This model was used for most of the simulation experimentation, as cellulose was used as an experimental model. The equation (34) directly represents the kinetics of cellulose complex decay.

7.2.2. Poisson Distribution Simulation Model
(time model 2)

If the time evolution of the decay process is assumed to be uniform, i.e. the probabilities of the fractional number of bonds breaking from the total population in any one of the outer time intervals or slices are assumed to be independent of each other, the inter event times (i.e. number of inner cycles) can be shown to be distributed according to a Poisson distribution (Walpole and Myers, 1978). In a MC method, the events are sequentially time-ordered. This implies that time elapsed to the next series of events from the start of previous one, can be determined from the randomly chosen sets of inner cycles, \(t(u)\). The latter consists of numbers of events that can be calculated either from the sum of hourly conversion rate contributed by the subset chain-length population or their averaging DP in each inner-cycle unit (Maksym, 1988).

7.2.2.1. Time-cycles as a Poisson Process
The polymer bond decay phenomenon can be compared to a radioactive disintegration, where decay of different atom occurs at randomly chosen instants. The times of occurrences are independent of one another.
Chapter 7: Simulation of Real-Time & Kinetics

(Yankovsky, 1969). It can be shown that the numbers of bonds breaking in any one-time event during a time interval \((0, t)\) can satisfy fundamental conditions of a Poission distribution as follows:

i. Stationary
ii. Without any after-effect
iii. Ordinary

Stationary signifies that for any group of a finite number of non-overlapping time intervals the probability of occurrences of a definite number of decays during the course of each one depends on the number of bonds broken and on the duration of the time intervals, but is not changed by an identical shift in all the time intervals. In particular, the probability of occurrences of \(k\) decays of bonds during the time interval from \(T\) to \((T, T + \Delta t)\) is independent of \(T\) and is a function of \(k\) and \(\Delta t\). The logic of this assumption can be well understood from the analogy with radioactive disintegration. Various disintegrations of atoms occurring in a comparatively large mass of a radioactive substance exhibit mutual independence in non-overlapping time intervals. The probabilities of occurrences of a certain number of decays have been shown to only depend on the length of the time interval and not on its location in time (Yankovsky, G., 1969). Although the relative mass diminution in size naturally may affect the reactivity or radioactivity of the substance but for comparatively small time intervals this changes can be regarded as insignificant.

The absence of after-effect means that the probability of occurrences of \(k\) decays of bonds during the time interval \((T, T + \Delta t)\) does not depend on how many times the decays occurred previously or how they occurred. Thus this signifies mutual independency of the occurrence of any number of decays during non-overlapping intervals of time. This assumption means that the conditional probability of occurrences of \(k\) decays during the time interval \((T, T + \Delta t)\) independent of any assumption of the occurrences of events prior to time \(T\).
Ordinariness expresses the requirement of practical impossibility of more than one decay occurring during a small time interval $\Delta t$. The condition of ordinariness is given in the following expression.

$$P_{\omega}(X > 1) = 0(\Delta t) \tag{35}$$

Where $X$ = the number of decays of bonds and $P_{\omega}(X > 1)$ denote the probability of occurrence of more than one decay in the time interval $\Delta t$.

In the case of polymer bond disintegration, the immediate problem will then be to determine the probability $P_i(X = k)$ that during an interval of duration $t$ there will occur $k$ decays. From the above it can be assumed these probabilities do not depend on the location of the time interval. For a small time interval $\Delta t$ the following equation holds.

$$P_{\omega}(X = 1) = m \cdot \Delta t + 0(\Delta t) \tag{36}$$

Where $m$ is a constant.

Consider a time interval of duration 1 and denote $\rho$ be the probability of no decay will occur within this period.

$$\rho = (P_{1/n}(X = 0))^n \tag{37}$$

Partition the time interval into $n$ overlapping equal parts. By virtue of stationary and the absence of after-effect clauses the following expression will hold. (37) can be expressed as follows.

$$P_{1/n}(X = 0) = \rho^{1/n} \tag{38}$$
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Through some intermediate steps it can be shown $P_t(X=0)$ satisfies the following inequalities from equation (38).

\[
\begin{align*}
\rho_n^{-k} & \geq P_t(X=0) \geq \rho_n^{-k} \\
\text{........................... (42)}
\end{align*}
\]

Taking the limit $n \to \infty$ the following inequalities are obtained.

\[
\begin{align*}
P_t(X=0) & \geq \rho' \text{........................... (44)}
\end{align*}
\]

Since $P_t(X=0)$ being a probability must satisfy the inequality

\[
0 \leq P_t(X=0) \leq 1 \text{........................... (45)}
\]

Three cases are possible:

\[
\begin{align*}
(1) & \rho = 0; \\
(2) & \rho = 1; \\
(3) & 0 \leq \rho \leq 1 \text{........................... (46)}
\end{align*}
\]

Only the third is of interest, which can be further developed as follows.

Let's suppose $\rho = e^{-m}$, $m \geq 0 :. m = -\ln \rho, \ 0 < e^{-m} < 1$

Assuming the assumptions of stationary and absence of after-effect as proven above the following equation is obtained for any time $t$

\[
\begin{align*}
P_t(X=0) &= e^{-mt}, \ t \geq 0 \text{........................... (47)}
\end{align*}
\]

Thus clearly (45) and (46) yields the following equation

\[
\begin{align*}
P_t(X=0) + P_t(X=1) + P_t(X>0) &= 1, \ \forall t, t \geq 0 \text{........................... (48)}
\end{align*}
\]

It follows from (35), (36) and (48) that for small $t$

\[
\begin{align*}
P_t(X=0) &= 1 - mt + O(t), \ \forall t, t \geq 0 \text{........................... (49)}
\end{align*}
\]

Now (49) can be followed for the probabilities $P_t(X=k), k \geq 1$
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For this purpose, we determine the probability that during time \((t + \Delta t)\) decay will occur for exactly \(k\) times. This may occur in \(k+1\) different ways, namely:

1. During time interval \(t\) all \(k\) decays will occur, and none will occur during time \(\Delta t\).
2. During an interval of length \(t\) there will occur \(k-1\) decays and one will occur during time \(\Delta t\).
3. During an interval of length \(t\) there will occur no decay but during time \(\Delta t\) the decay will occur \(k\) times.

Considering \(k\) cases of occurrences, the total probability will result in the following summation, where events occurring in time intervals \(t\) and \(\Delta t\) are independent of each other (applying condition of stationarity and absence of after-effect).

\[
P_{t+\Delta t}(X=k) = \sum_{j=0}^{k} \left( P_t(X=j) \times P_t(X=k-j) \right) \quad \text{(50)}
\]

Equation (56) is obtained through some intermediate steps from (50)

\[
P_{t+\Delta t}(X=k) = P_t(X=k) \times (1-m\Delta t) + P_t(X=k-1) \times m\Delta t + o(\Delta t) \quad \text{(56)}
\]

(56) can be written as,

\[
\frac{P_{t+\Delta t}(X=k) - P_t(X=k)}{\Delta t} = -m*P_t(X=k) + m*P_t(X=k-1) + o(\Delta t) \quad \text{(57)}
\]

Since as \(\Delta t \to 0\) the limit of both side of the equation (57) we get,

\[
\frac{dP_t(X=k)}{dt} = -m*P_t(X=k) + m*P_t(X=k-1) \quad \text{(58)}
\]

Equation (58) can be solved by making the following substitution and some intermediate steps of integration.
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\[ P_t(X=k) = e^{-mt} v_k(t) \]  

Where \( v_k(t) \) is the new desired function.

Substituting the general expression for \( k \) terms from (64) into (60),

\[ P_t(X=k) = e^{-mt} \frac{(mt)^k}{k!} \text{ for } k \geq 0 \]  

So for a particular time period \( t = \text{constant} \)

\[ \Rightarrow \text{ } mt = \lambda; \quad \lambda = \text{constant} \]

Equation (65) obviously presents the general form of a Poisson distribution. The detail of the application of the equation (65) to fit the cellulose and similar polymer kinetic behaviour is given in the appendix 6.

7.2.3. Use of Rectangular Hyperbolic Function  
(time model 3)

A parametric function to similar in form to one branch of rectangular hyperbola in the first quadrant of the coordinate axis was constructed from the second order rate equation as below.

\[ y = \frac{1}{k_1 t + k_2} \]  

Where \( k_1 \) and \( k_2 \) are constants and can be regarded as rate constants.

The following assumptions were required:

(a) The resultant of the reaction rates of the polymer subset components follow an approximation to second order kinetics and
as such the rate depends on the square of the initial concentration of the average DP.

(b) When the decay ultimately declines to a lower boundary – the limiting DP, the decay curve takes an asymptotic shape with respect to the x-axis. This implies that after reaching a limiting DP the decay continues with an infinitesimal rate.

(c) Ideally the other half of the curve should ultimately become an asymptote with respect to y-axis from some point above its focal point, which lies above the x-axis and along the parallel transverse line drawn through the limiting DP. This would mean there is no zero time starting DP implying that decay starts at a time that is closed to a finite time but never reaches it. In reality this is not possible, hence it is required to assume decay start at a finite point when time t=0 then x=0 and y=starting DP of the intact polymer.

(d) \( y = \text{DP}_t \) of the intact polymer at time t.

(e) It is assumed that the rate is dependent on the average molar concentrations of both medium and long chains, which the intact polymer is largely comprised of, before the start of the decay process. It is also assumed that only these chain lengths contribute to the scission process of the entire system in such a way that these two components of the macromolecular system act as two separate reactive entities. The latter can be imagined as two individual narrow polydisperse polymers.

(f) \( k_1 \) represents the main resultant rate constant and \( k_2 \) is a coefficient that preserves the shape of the curve with regard to the time that is plotted along the x-axis.
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(g) Along the y-axis are plotted the total concentration of the medium and long chain components (i.e. the remaining undegraded bonds following a decay cycle).

(h) $k_1$ is calculated from the equation (22) and (23) of section 5.4.2.2.

(i) $k_2$ is calculated from the initial condition of the polymer (i.e. initial total bonds) and (23) of the above section.

The above method can be hypothesised to be appropriately applicable for a complex polymer system with a broad polydispersity. In this thesis cellulose decay is exemplified. The advantage of this time calculation method over the exponential method (i.e. equation 34) is the ease of calculation and the ability to obtain a better decay curve with a definite point of inflection at the limiting DP. This method is tested in this project to show that it presents a better alternative to the Poisson distribution method to simulate an exponential decay curve as obtained from the cellulose lab-test.

Alternatively, the temporal decay process can be represented as a Markov process whose random walk can be imagined to traverse in a conical orbital in infinite time and space. The outcome sample points remain within this envelope such that a cross section of the latter would yield a rectangular hyperbola. The focal point of this rectangular hyperbola will always be the limiting DP of a polymer system at or around which the path of decay will take a radical change that can be compared to the similar change in direction of the exponential decay characteristic. The point of inflection can easily be determined from the curve and from it the limiting DP at different temperatures from which it is possible to deduce a life prediction curve.
7.2.4. Random Geometric Distribution
(time model 4)

The way this time model carries out the simulation of bond scission process is quite different from the other degradation and time simulation models, so far described. In the others, time progression is considered as a completely independent process that depends on the number of bond breakages. Decrease in total bonds in a degradative reactor is assumed to be dependent on time. For example in the case of cellulose, the degree of polymerisation (DP) was worked out on the basis of total number of bonds broken within a particular time cycle, which was assumed to be a proportion of the total time. The number of bonds that could be broken in a given time for each chain length category from the entire chain population was considered for each time series. In contrast, each category of polymer molecular chain can be considered separately at each progression step of the algorithm. Then the pieces this chain can be broken into can be defined. The distribution of fragments of each chain species can be worked out for a fixed time range of the total decay in the following geometric distribution fashion.

Let's isolate a fixed chain \(i\) from the entire chain lengths \(i=1,2,...,n\). for a fixed time \(t\) the fragments \(G_1, G_2, G_3,...\) can be simulated with parameter \(e^{-bt}\) following a random geometric distribution of probabilities \(P(G=i)\).

\[
P_t(G=i) = p \cdot (1-p)^{(i-1)}; \quad p = 1 - e^{-bt}; \quad \sum_{i=1}^{n} G_i = n \quad ......(78)
\]

For a polydisperse system with \(n\) category of chain species the above can be applied for each subsequent series in the algorithm for a fixed time \(t\). This model presents a very simplistic way to derive the direct calculation of possible and expected distribution of the generated fragments for a given time from the initial starting chain length distribution \(d(n,0)\). The parameter \(b\) describes the rate at which each link breaks and is arbitrary. Varying \(b\) for different chain categories would achieve an outcome similar to the
preferential scission models described in this thesis. This model was tested and the outcome was found irreproducible due to its very random nature and also its application was found to be only suitable for simple scissions. This algorithm may very well describe the disintegration behaviour of a purely first order reaction, but was unable to effectively describe complex degradation, such as cellulose. However, it was included in the time distribution model because the number of fragmentation describes a pattern of time distribution, which is inherent in the process (Fig. 7.1).

7.2.5. Comparison of Time Rate Curves
(Fig. 7.2 a-d)

An example of individual bond scission rate profiles (decay of cotton linters 120°C), calculated from the time model 2 i.e. Poisson distribution (Fig. 7.2 c-d) and time model 3 i.e. rectangular hyperbolic function (Fig. 7.2a-b) are presented in Figures 7.2 a-d exhibit deviation from linearity. Rate curves obtained from both time models (Fig. 7.2a and Fig. 7.2c) display an exponential decrease in the average DP (pink and green dots distinguishing time models 3 and 2 respectively) calculated from the estimates of the unbroken bonds (green dots and yellow dots distinguishing time model 3 and 2 respectively) remained following the main degradation cycle in a sequential order, which yet retained an approximate linearity. This is due to the non-linear increase in the number of generated chain fragments over each time interval or cycle. The time model 3 calculation that was based on unbroken bonds as rectangular hyperbolic function of time shows closer profile to that obtained from the time model 1 (results given in Chapter 6) than the same exhibited by time model 2 that represents number of bonds broken per unit time cycles as Poisson distribution. Despite of an apparent linear decline of integral unbroken bonds displayed by both models in sequential manner, however their average values preserved exponential nature that is unique of cellulose molecular average decay kinetics. This shows that both models can be applicable to describe complex molecular
Poisson (Fig. 7.2a-b) and Hyperbolic (Fig. 7.2c-d) time-function derived bond scission kinetics

**Fig. 7.2 a-d**

*Rate Curves*

*Total Bond Mobilisation Vs Time*
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decay. However, further investigation is required to find the above models' individual suitability to the type and nature of polymers in general.

The nature of intermediate extent of reaction and total bond mobilisation displayed by model 2 (Fig. 7.2d) is different to that of model 3 (Fig. 7.2b). Both percent (pink dots in both cases) and rate graphs (green dots in both cases) of the former displays a 'S' shape with a noticeable slower rate of decay progress, particularly at the initial phase, in contrast to a much faster rate displayed by the latter model in reaching a final saturation point. The time model 3 also shows a faster increase in percent bond mobilisation during the period of early to mid phase of decay compared to those obtained from model 2. Hence a pronounced peak was observed in the former profile by 1/6th of the total decay time in the percent graph, which took almost half of the total decay time in the latter. This may indicate Poisson time distribution model (model2) would be more suitable for enzymolysis of polymer that often displays this particular 'S' shape until the reaction reaches a saturation time. The latter is often follows a zero order kinetics. The rectangular hyperbolic function of bond mobilisation over time, on the other hand, may be more suited to describe a non-linear type of reaction kinetics that is more evident in pseudo-first order or second order kinetics.

7.3. Death Model (Fig. 7.3 a-b)

A new way of designing the algorithm is shown in Fig. 7.3a-b, to generate a simulation for a large time T. Fig. 7.3a shows a binary tree diagram, which reflects a death pattern for each individual molecule over the extent of a decay process, that ultimately leads to death through continued central or end cleavage. Fig. 7.3b presents an algorithm of this death process, which assumes each molecule breaks into two equal or unequal parts at each step of dissemination of death. \( D(l) \) defines a time for death of a molecule of chain length \( l \) and \( S \) represents the death time that goes on proliferating until the complete death is reached. In this model \( S \) is imagined as a time particle, which grows gradually accumulating the magnitude of a death time.
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Binary Tree Death Algorithm for Molecular Scission Process

**Fig. 7.3 a-b**

**Binary Tree Death Diagram:**

<table>
<thead>
<tr>
<th>0</th>
<th>1</th>
<th>2</th>
<th>....</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>....</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_r11(l/4)</td>
<td>D_r1(1/2)</td>
<td>D_r12(l/4)</td>
<td>D_r1</td>
<td>S_r1</td>
<td>S_r12</td>
<td>S_r121</td>
<td>T</td>
</tr>
<tr>
<td>S_r121&gt;l/T</td>
<td>S_r12&gt;l/T</td>
<td>S_r121&gt;l/T</td>
<td>S_r12&gt;l/T</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Chain Division Binary Tree Time Distribution**

**Input I (chain length) and T (total death time for I)**

**Generate D(l)- the time to divide I into two fragments if r (r=2,3,...)**

**Death Algorithm**

1. Check if \( I_{r1} = D(l/n) > T \)?
   - yes
   - no: Add \( D(l_{r1}) \) to \( S_{r1} \)
   - Check if \( S_{r1} > T \)?
     - yes: stop
     - no
2. Check if \( I_{r2} = D(l/n) > T \)?
   - yes
   - no: Add \( D(l_{r2}) \) to \( S_{r2} \)
   - Check if \( S_{r2} > T \)?
     - yes: stop
     - no
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series until it bursts i.e. until the chains cease to exist. The time \( T \) is fixed for each particle death time. However, particles can reach death before this time and so the end-point of a chain category can be reached at any point along the binary tree of chain fission events. \( D(1) \) represents the time for a chain particle to divide into two daughter generations, but this mathematically means the death of 1 chain, which ceases to exist at the time of division. The binary tree graph thus illustrates a unique new concept of molecular death time distribution.

7.3.1. Mathematical Interpretation

At stage \( n \), let's consider there are \( 2^n \) elements, all of which are of length \( l \times 2^{-n} \) where \( l \) is the original length of the chain. The roots of the tree are labelled as \( r \) and each node in the graph as a sequence of 0's and 1's. For example, the first element is \( r \), it has offspring \( r_1 \) and \( r_2 \) and \( r_1 \) will have offspring \( r_{11} \) and \( r_{12} \) etc. The tree graph of real time can dictate when each particle exists. The *'s in the diagram Fig. 7.1 represent time particles whose distribution can be simulated using a probability density curve of the sort shown in Fig. 7.1. The algorithm Fig. 7.3b will allow us to read from the graph, when each particle lived, and the number of chains of length \( l^n \) which are alive at time \( t \). For example, a particle \( r_{1211} \) is alive at time \( t \) if and only if:

\[
D_r + D_r1 + D_r12 + D_r121 < t < D_r + D_r1 + D_r12 + D_r121 + D_r1211
\]

Where the tree is simulated for all times \( t<T \).

The number and lengths of all chains existing at time \( t<T \) can be easily read for all times \( T \), e.g. \( r_2 \), \( r_{122} \), \( r_{121} \) and \( r_{11} \) are the particles alive at time \( T \). This model allows the distribution of the duration of time taken for each chain to die to be specified more freely, without increasing the overall complexity of the computer algorithm. \( D(k) \) can be assumed exponential (a Markov chain assumption). The different ways that the \( D \)'s can be distributed using Gamma or Geometric random variables can be determined from Fig. 7.1. However, time distribution patterns can vary from polymer to polymer as
well as from one subset of constituent species to another. The death
algorithm can be particularly used in finding the end-point of those chain
species responsible for maintaining the mechanical strength e.g. tensile,
 elongation etc. This model also simplifies this search by considering each
individual mono-disperse system at a time rather than dealing with a
polydisperse one.

7.4. Processing of Kinetic Results

A brief introduction is given next to thermodynamic parameters, which
govern the rate-limiting stage of a reaction.

7.4.1. Important Kinetic Parameters

The thermodynamics and kinetics of a chemical reaction may be expressed
in terms of thermodynamic equilibrium or Gibbs free energy equation or
activation energy derived from Arrhenius equation. In most cases of polymer
kinetics the Arrhenius equation is commonly used to determine the rate
constants. The Arrhenius equation is as follows:

\[
\ln k = \ln A - \frac{E_a}{RT} \quad \ldots \ldots (79)
\]

Where:
K = rate constant, T = absolute temperature (Kelvin), R = gas constant
(8.314 JK\(^{-1}\) mol\(^{-1}\)), \(E_a\) = activation energy, \(A\) = pre-exponential factor.

A plot of \(\ln k\) Vs \(1/T\) is supposed to be linear where the co-efficient \(E_a/R\)
characterises its slope and \(\ln A\) the intercept of the equation (1).
Collectively, the two quantities \(A\) and \(E_a\) are called Arrhenius parameters
that provide the important kinetic information to the behaviour of a course of
reactions at different temperatures. The values of both may vary significantly
for a complex system such as cellulose decay.

The above can be written in Gibbs energy form and compared as below.
\[ k = A e^{\frac{E_a}{RT}} \qquad \text{(80)} \]
\[ k = A e^{\frac{DG}{RT}} \qquad \text{(81)} \]

\( \Delta G \) is called the activation Gibbs energy and depends directly on the entropy of the reactor. Thus the expression for the rate constant in (2) strongly resembles the equilibrium constant in (3). Both interpret the variation of rate constants with temperature. The pre-exponential \( A \) has been shown to be very sensitive to any change in the reaction environment or type of substrate in the present study of cellulose. The detail of how the above Arrhenius parameter values were obtained from the lab-experiment is documented in the thesis of Heywood (1997). Similar tables containing the values for Arrhenius parameters obtained from the current simulation models will be included in the following main section.

### 7.4.2. Implications of Entropy and DP of Cellulose

Though for simplicity DP is used in kinetic measurement as representative of the entire chain population, in practice it refers to the chain category having the highest frequency for a time subset during the course of decay. The rate of decrease in this average chain size attribute was used in the kinetic rate equation in order to derive Arrhenius kinetic parameters in both cases of simulation and lab-experimental study.

In the case of solid phase reactions the speed of reaction not only depends on the state and energy differences of the reactive cross section enveloping the configurational distortions of the reactant complexes it is also governed by the internal entropy of the reactor system. The latter may vary hugely during the course of slow partial degradation reactions in a closed reactor such as electrical transformer, where the accumulating products (e.g. moisture) can act as degradative agents and accidental electrical circuit errors can spark the rise of heat that can act as catalyst. In case of solid phase reaction of cellulose, the degradation rate thus depends on multiple factors...
factors inherent of the reactor system. For example for reactions in air, the rate depends on diffusion of oxygen, whereas in an oil medium it may depend on the diffusion of moisture. In addition, the heterogeneous presence of other impurities in the system may bring a substantial change in the entropy of the system. A critical review of numerous lab-experimental studies by Emsley (1994a, b) set an average value of $E_a$ as $111 \pm 6$ KJ/mol. The stability of this range has been experimentally verified by both lab-experiment (Emsley and Heywood, 2000) and the present simulation results (Tables 7.1 and 7.2) and was used by Emsley and Heywood to extrapolate to normal transformer operating temperatures. DP vs. time curves were fitted using a numerical modelling package (Model Maker from Cherwell Electronics Ltd). Arrhenius parameters were calculated from DP data calculated from the simulation experiments reported in chapter 6 using the same kinetic models and the results are reported next.

### 7.5. Kinetic results from the Simulation Experiment

#### 7.5.1. Comparison with Observed Results

(Tables 7.1-7.2 & Fig. 7.4 a-f – 7.5 a-g)

Table 7.1 presents the Arrhenius parameters $A$ and $E$ (where $A_1$ and $E_1$ were calculated for the initial rate constant $k_1$ and $A_2$ and $E_2$ for the rate constant $k_2$) for simulation models calculated using Slider, Markov and Algebraic maths and two different time models – exponential and Poisson. The original data were obtained from simulation model run from the simulation program yielding MWD curve sets for different environmental conditions (e.g. air and oil) and temperatures.

Table 7.1 shows that, although there is some scatter in the results, they are generally in good agreement to the observed values (Emsley and Heywood, 2000b).
### Table 7.1

**Arhenius Parameters for Cotton Linter Aging in different medium**

<table>
<thead>
<tr>
<th>Mathematical Model</th>
<th>Medium</th>
<th>Temperature $^\circ$C</th>
<th>$A_1$</th>
<th>$E_1$</th>
<th>$A_2$</th>
<th>$E_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slider Data</td>
<td>Oil</td>
<td>120</td>
<td>5.21E+07</td>
<td>100.5</td>
<td>2.16E+04</td>
<td>105.1</td>
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<tr>
<td></td>
<td></td>
<td>140</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>excluding recombination</td>
<td>Air</td>
<td>120</td>
<td>1.57E+03</td>
<td>79.9</td>
<td>2.16E+04</td>
<td>66.0</td>
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<td>160</td>
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<td>2.16E+04</td>
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</tr>
<tr>
<td>excluding recombination</td>
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<td>Poisson Data (Slider)</td>
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### Table 7.2

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<th>Temperature</th>
<th>Effect of $H_2O + O_2$</th>
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<th>low $H_2O + med O_2$</th>
<th>med $H_2O + med O_2$</th>
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<td>$120^0C$</td>
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<td>1.636E-06</td>
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<td>5.075E-06</td>
<td>3.954E-06</td>
<td>6.822E-06</td>
</tr>
</tbody>
</table>
Chapter 7: Simulation of Real-Time & Kinetics

Pre-exponentials were presumed to be higher in air than oil owing to the increase in degradation rates in air (Emsley and Stevens, 1994). Markov and Poisson models exhibited this. The high fluctuation in $A_1$ values was unexpected as there were few significant differences in the original data sets obtained from different simulation models. This may be due to a limitation of Model Maker program, which may not be accurate enough with the limited data provided. However the activation energy ($E_1$ and $E_2$) values are within an order of magnitude of the observed values.

Table 7.2 presents Arrhenius parameter rate constants ($k_1$ and $k_2$) values from the simulation results for the ageing of cotton linters under different conditions of $\text{H}_2\text{O}$ and $\text{O}_2$ and heat i.e. temperatures ($120^\circ\text{C}$ and $140^\circ\text{C}$). These effects were critically examined in Chapter 6 and also showed a reasonable agreement to the observed values (Emsley et al., 2000a).

The figures 7.4a-f and 7.5a-g further display the closeness of simulation results using a wide variety of modelling methods, introduced in this thesis, to those of observed graphs. These graphs were obtained from Model Maker run by Dr. Emsley from the original data obtained from the simulation program.

These initial findings demonstrate the potential for using the computer simulations to calculate kinetics parameters, but further work is required in respect of both lab-experimental and simulation-experimental investigative studies to achieve better agreement between the two.
Kinetic Results from Simulation (Poisson Time Model)

Fig. 7.4 a-c

Poisson Slider Oil, $E_1=100.5$, $A_1=4530406$

Poisson Slider Air, $E_1=79.9$, $A_1=55609$

Poisson Maths Air, $E_1=58.5$, $A_1=99.5$
**Kinetic Results from Simulation (Poisson Time Model)**

Fig. 7.4 d-f

Poisson Maths Oll, E1=121.7, A1=5193106918.81441

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Poisson: Effect of H2O and O2 at 120°C

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Poisson: Effect of H2O and O2 at 140°C

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Chapter 7: Simulation of Real-Time & Kinetics

Kinetic Results from Simulation (Exponential Time Model)

Fig. 7.5 a-c

Cotton Linters Air, Slider model E1=138, E2=140

Cotton Linters Markov (with recombination) Air E1=45.0, E2=11.1

Cotton Linters Oil, Slider model E1=165.0, E2=235

---
Kinetic Results from Simulation (Exponential Time Model)

Fig. 7.5 d-e

Maths Air $E_1 = 48.1$, $A_1 = 5.72$

Maths Oil $E_1 = 81.8$, $A_1 = 80392$
Kinetic Results from Simulation (Exponential Time Model)

Fig. 7.5 f-g

Slider Model: Effects of $\text{H}_2\text{O}$ and $\text{O}_2$ at 120$^\circ$C

Slider Model: Effects of $\text{H}_2\text{O}$ and $\text{O}_2$ at 140$^\circ$C
7.6. Conclusions

- The simulation experiments show that time progression of degradation and its kinetic behaviour can only be truly monitored from the number of bonds breaking per unit time or per each reaction extent. In this respect, a well-defined scheme of distribution of time subsets is required that depends on the characteristics of the reactor as well as the polymer system.

- The time model 1 is primarily used in this thesis and is directly based on the kinetic equation (34) derived from the lab-experimental tests that simulated accelerated ageing conditions for an electrical transformer where cellulose is used as insulator.

- However the above equation has limitations. It is only valid for a certain range of DP values, beyond which the equation exponents become infinite or it is not valid.

- In order to avoid the above problem other statistical time distribution methods such as classical Poisson (time model 2) and random Geometric (time model 4) were investigated. In addition to these two alternative approaches, a derivative of Rectangular Hyperbolic function (time model 3) was deduced to evaluate subsets of time that would more directly correspond to real time (hourly basis) and the DP relationship achieved by time model 1.

- It was found that time model 3 was the best suited to the very exponential nature of cellulose disintegration kinetics. This model was designed to accept the number of undegraded bonds in place of DP at the end of each time cycle of degradation. This was found to be more sensitive to yielding real time values than using DP values only.

- DP values are discrete integers, which can vary significantly between consecutive time series. This was difficult to compensate for and as such made the time values inconsistent in some cases of simulation sampling (e.g. the DP sometimes increased with time).

- The problem could be eliminated by the use of the number of undegraded bonds, which is a real number, but this did not provide the
rate constants $k_1$ and $k_2$ for cellulose kinetic profile, which were available using time model 1. Hence time model 1 is used for most simulations and time model 2 or 3 were only used when model 1 became invalid.

- Time distribution models such as 2, 3 and 4 are still included, as they may prove useful for other polymer systems in future studies.

- The kinetic parameters from the Arrhenius equation were obtained from the different simulation models using time model 1 and 2 and were compared with those from lab-experiment of cellulose-accelerated tests. The both sets were found to be in good agreement with the latter.

- A similarly good agreement was obtained between the simulation and observed kinetic results for the degradation cases where the proportions of degrading agents were varied.
Chapter 8

Conclusions and Discussion

8.1. Conclusions and Discussion

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   8.2.2. Introducing Probabilistic Static Monte Carlo Method
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8.1. Conclusions and Discussion

This thesis has shown a novel way to approach and develop effective and powerful simulation strategies of polymer degradation by combining mathematical models with computer window interface techniques. The former has provided simulation experimental protocols, and the latter has served as an experimental tool to define the parameters. A macromolecular polysaccharide – cellulose has been studied in depth as an instance of a linear polymer decay mechanism.

New mathematical approaches have been developed in order to capture complex reaction strategies of macromolecular decay processes and computer software has been developed and modified to efficiently incorporate these strategies with ease. A variety of interactive interfaces equipped with resourceful window menus have been designed and implemented in order to incorporate many important functionalities integrated with essential parameters and attributes into the process of developing the simulation methods and strategies. Conclusions will be drawn for each stage of a stepwise development and suggestions proposed for further future work before ending with an overall synopsis of the inferences derived from simulation experimental results.

8.2. Optimisation of Simple Scission Models

The processes of degradation can be imagined as a spectrum of possible reactions, evolved in a random fashion that results in a series of "polychromatic" kinetic processes. Differences arise in the scission strategies due to "neighbouring" effects, configurational and conformational effects, steric hindrance, limiting permeability, effects arising from differential aggregation densities and polymer phase density and many others. A number of simple scission mechanisms were refined in order to define these differences as well as to represent various modes of degradation such as thermal, chemical, photochemical, thermo-chemical, radiation based etc.
(described in Chapter 2). A simulation study of cellulose decay defined the suitability each individually or in combinations as models of the degradation processes. For example 'Unzip' mechanism can be used to portray radical initiated reactions, 'CutFixedlength' to portray thermal-hydrolytic reactions, whereas a combination of 'Unzip' with 'Weaklink' can portray initiation at some location for a chain rupture and thus build a nucleation centre.

8.2.1. Enhancing Software Output and Graphic Features

The initial model developed by Emsley and Heywood (1995) used an iterative random algorithm that uses simple random number generation and was devoid of any robust probability structure to enable to portray MWD curve features and shift characteristics. The initial software program was also lacking in suitable graphic output and user-friendly interfaces and various other functionalities. The first phase of development in this project was mainly devoted to developing the computer program to a satisfactory standard to enable the preliminary simulation investigation with the simple models.

8.2.2. Introducing Probabilistic Static Monte Carlo Method

Several modes of chain cleaving mechanisms such as 'Cutpercent', 'Unzip', 'Weaklink' etc. were harnessed with probability-governed algorithms in order to portray a chain rupture event. The initial simple scission models assumed that all chains, comprising a polymer matrix, were equally liable to attack by a degradative agent and did not account for any structural or configurational differences. Similarly it assumed a randomly selected chain could be cleaved at any bond location along the backbone. In reality this is not the case. Chain sites or bond locations in a macromolecular complex assembly are not necessarily equally probable to cleave over a prolonged partial decay situation. The probability of reaction rates thus varies enormously from one time segment to another and is a function of structural, thermal and degradation zone parameters, as shown by McDermott et al. (1990) and
Rapoport and Efros (1994) in their computer simulation of degradation of synthetic polymers.

Thus variability of different related factors can be simulated by means of different sets of non-uniform weighted probability density functions. A few probability-weighting algorithms (such as skew, geometric, normal etc.) on the molecular size selection process were tried to achieve progressive curve shift from HMW to LMW region and the MWD curve features. But these were not successful. Finally, a composite distribution function attaching variable probability weights depending on the location of the molecular species coming from different chain assembly or 'strips' was found efficient. The function is made of arbitrary density components such as height / depth and probability units $\alpha_k$, can be defined as respective areas partitioned by different sized rectangles. So the probability density with more depth will earn priority at the time of random selection. This was further developed later in the project, into a more robust probability structured Slider model, with the aid of computer interfaces. The latter incorporates a random sequence of statistically independent samples from given probability distribution functions of possible states. The latter defines the status of a polymer chain component and its reactivity. The state $E_k$ occurs if the following inequalities hold:

$$\sum_{j=1}^{k} p_j < x < \sum_{j=1}^{k+1} p_j$$

This step is repeated as many times as required and the inequality is stipulated by a few restrictions of boundary condition as demanded by the above functions. This strategy enabled the composition of a framework of Monte Carlo static models. At each turn of a unit time cycle, the choice of a chain population can thus be made preferential to some extent in order to favour the gradual progression of the lateral shifts.
8.2.3. Introducing Curve Smoothing Algorithm

The very discontinuous nature of probability manipulation over the whole range of chain population enforced some other kind of interference, causing interruption in maintaining the continuity in the curve contour. Since the Monte Carlo simulation method involves large numbers of random repetitive phenomena the ultimate calculation causes severe irregularity in curve geometry. This leads to obscurity and misleading interpretation. To maintain the accurate smooth curvature is not an easy task.

This was overcome with the help of a curve-smoothing algorithm to compensate for any apparent disparity or divergence in plotting data coordinates. An efficient smoothing algorithm has been investigated and Cubic Cspline was found most suited to operate on a large number of data points as in the current simulation exercise. The algorithm uses a polynomial interpolation of the graphic coordinates, extended over a large area to recover the actual form and direction of the curves from their longitudinal divergence of data points which fluctuate within large amplitudes.

These graphical surveys also specifically provide information on the polymer structural issue. Polydisperse polymers are usually composed of intricate orders and levels of structural organisation that influence the resultant degradation behaviour. Thus clarity in plotting a series of subsequent intermediate MWD curve shapes, exhibiting temporal decay pattern and extent of decay, is important, as each helps in interpreting the corresponding temporal state of reaction and regional progress.

8.3. Development of the Software Program

A basic software program, originally initiated by Dr. Emsley at UniS, is further developed in this project in order to perform large-scale simulation experiments. The program is written in object oriented programming (OOP) language under MFC Visual C++ programming platform (Microsoft).
Separate individual parent classes for scission models and graph plots could have been introduced. The individual common properties and functionalities of the scission models were then encapsulated in a new parent class - 'Cmodel', which thus facilitated inheritance of common properties to its child or relative classes. The branched child classes in turn were further structured with the additional provision of their individual characteristic differences in properties. The same class ordered design was also introduced for the graph plots for each separate simulated attribute.

The class structure has been expanded in the developed program infrastructure that serves as the main body of the program. Provisions of new parent and friend classes have been made for a variety of functionalities and user-friendly window interfaces added which are described in detail in Chapter 5. This has strengthened the program performance and speed. Some of the main features are outlined below.

### 8.3.1. Architectural

- There are 3 main outlet and inlet fronts – user input front, the graphical display outcome front and various intermediate fronts providing the user with various options of further “Data Processing” stages within the program architecture. User input data undergoes transformations necessary to conform to desired outputs at the user output front. The latter displays simulation results and charts and so requires to be presented in multiple view windows, for clarity and comparative study. This is achieved by invalidating the window’s client area, which triggers the disappearance of the previous image and repaints it with a newly chosen plot from a window menu. Splitter window applications could be introduced as a further refinement.

- Experimental MWD data (both for lab and simulated) reading from an external file and storing in the array variables to review their outcomes (graphic and charts) in the output window was implemented. Similarly,
provisions for storing the simulated data in external files were implemented. This aided the formation of a database record for various trends of simulation results for future use.

- Data and their function encapsulation is an important feature in 'Object Oriented Program (OOP). Most of the important methods and complex models, derived in the project, were implemented in the form of an individual 'Class' (e.g. 'Cexppar', 'Cslider', 'CpolydegMC'). The latter are provided with their own individual interfaces, which collect various data and their simulation functions in the form of commands from the user and preserve the multiple data objects in class's infrastructure.

### 8.3.2. Interfaces

There are a variety of interfaces added as functional tools. Some of the main interfaces are listed below:

- **Menu Interface** – serves as the main parent window interface providing a variety of program menus for the user to access some of its fundamental functionalities and the options for selection of type of degradation model run, graph plot, data-chart/parameter-table plot, statistical outcome, dimension and number of graphic display. To start with experimentation, user need to first access data and command input interfaces such as 'Data Entry' and 'Experimental' and for more complex model run these can be followed by 'Slider I' and 'Slider II' interfaces and so on.
- **'Data Entry' interface** – serves as the primary data input stage. It receives values for several categories of parameters, such as scission model attributes, graph plotting attributes, mode of PDF selection, time calculation functions, graphic display formats etc..
- **Interfaces to Save and Load Files**—each sample attributes for a simulation experiment are saved in a "par" files, a text file for storing data for future use. When, in future, this particular file is selected for loading, the values will
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be transferred to the respective parameter variables as displayed by various control boxes in data-entry dialogue box.

- ‘Save ndata as’ Interface—dumps the content of ‘ndata’ array that stores the degraded chain distribution data for a desired number of time-cycles, generated by a simulation experiment sample run, in an external file. Similarly, output data from other related graphs and parameter tables could be stored in an external file from their individual data structure, used in the program. The data can then be retrieved from this external file into an excel file for the necessary utilisation or can be loaded back into the program from the external file via ‘Experimental’ interface for instant re-plotting of the stored MWD sample without having to go through the steps for a new degradation sample run.

- Experimental Data Interface—serves to read and import pre-saved experimental (both lab and simulation) chain distribution data from an external file and store it in order in a ‘Listbox’ for re-processing by the program to review the graphical output.

- ‘Data Rendering’ Interface—abstracts data from the graphic routine used for plotting, so that one/some of the selected distribution curve/s can be hidden from the display output. This eliminates crowding of sets of overlapping curves in the view window and helps close examination of the contour of the curve / curves of importance.

- Slider Model interfaces (I and II)— receives various parameters at the user front for processing input data using MC dynamic style model run. Slider I interface also performs a complex network of scission models that can be used by both MC slider dynamic model and mathematical algebraic exact models.

8.3.3. Speed

The computer run-time for initial models at the beginning of project demanded about 50 minutes to 1 1/2 hour to run 5-10 number of outer decay time cycles for the iterative models, using 386 processor and 40MB of
memory. Following the above optimisation and enhancement of the algorithm the runtime was cut down to almost one third.

The current optimised program would take a maximum of 10 minutes to run a Slider model sample that involves 15-20 number of outer decay time-cycles with largest extents of inner-cycle units using Pentium 4 processor of 1000MB disc capacity and 100MB memory. The instant calculation of mathematical models such as Markov chain probability matrix are the fastest of all, taking no more than 2-5 seconds of runtime, whereas algebraic maths model would take 10-20 minutes for the same duration of decay.

8.4. Complex Scission Models

8.4.1. Method Development with Computer Aided Strategy

Individual use of simple scission models is not adequate to mimic a complex decomposition reaction. An algorithm incorporating several layers of probability structure was required with a view to recreating all the possible variations in kinetic rates in the simulated reaction strategies. The ability to initiate nucleation centres among the various structural domains was found to be necessary to simulate a complex reactor. For this a number of mathematical models were critically investigated. This enabled the generation of much clearer molecular weight or chain length distribution graphs of the temporal changes in the MWD curve set in keeping with the evolving molecular dynamics in the decay process. Cellulose was chosen as the subject of this decay study, as an example of linear polymer undergoing slow and partial decay processes.

The variability experimental reaction rate (in cellulose for instance) indicates existence of differential reactivity amongst the constituent chain subsets owing to their variable molecular sizes and most importantly structural rigidity. It is important to understand and define the causes behind this
deviation in the rate constants at the molecular level that can only be discerned by examining polymer molecular chain fragmentation process more closely. Computer aided mathematical modelling has been shown to be a powerful technique for investigating this problem in this thesis. The mathematical models, developed successfully in this project to describe molecular chain fragmentation processes more closely (and described fully in chapter 5) are highlighted next.

8.4.2. Incorporation of MC Dynamic Method
Using Slider Interfaces as a Vehicle

This model used two separate computer aided strategies incorporated in Slider I and II Interfaces (described in Chapter 4 and 5). Both incorporate two levels of probability algorithms (rectangular and triangular PDF) and the data variables required for simulating variable environmental conditions of a complex thermo-reactor. The following probability functions were developed to control the occurrences of variable scission events and nucleation of a degradation zone per each time cycle throughout the total decay time.

\[ \omega(n,t) = \int_{s_l}^{s_i} \frac{d(n,s)}{T(t)\lambda_2} \psi(n,s) \lambda_1, \quad 2 \leq n \leq N, \lambda_1, \lambda_2 \text{ = weights} \]

\[ \psi(n,s) = \left[ \int_{s_{i-1}}^{s_i} \psi(S) \left\{ n \left( \frac{1}{T(S)} \right) \right\} ds, \quad 0 \leq t < \theta \right. \]

Where \( \omega(n,t) \) \( \Rightarrow \) represents the weighted probability function of \( n \) (chain sizes) and \( t \) (time). The RHS expression involves \( \psi(n,s) \) specifying a function of chain length and subset range parameters. This function expression is given above in differential form on the subset range that is bounded by two finite limits (lower and upper) accounting for the entire molecular population. \( \lambda_1 \) and \( \lambda_2 \) are constant coefficients for the fine adjustment of a converted continuous probability density chain, calculated...
from the user given discrete slider weights in the interface, to work efficiently.

b) Rectangular

\[
\omega(n,t) = \frac{(Y_b - Y_i)}{(X_b - X_i)} \ast \left(\frac{1}{X_i} \ast X_i \ast \lambda_i\right), \quad 2 \leq n \leq N, \quad A_i = (X_i, Y_i), \quad B_i = (X_i', Y_i')
\]

Where \( \omega(n,t) \) represents the weighted probability function of \( n \) (chain sizes and \( t \) (time). The RHS expression involves \((X_i, Y_i)\) co-ordinates of the adjacent weight points at \( A_i, B_i \) ..... locations in the Slider II interface, where \( i \) refer to the number divisions of polymer molecular chain subsets. \( X_i \) specifies the chain size intervals and \( Y_i \) the upper limit of the allocated weight in that interval. \( P(S_i) \) represents comparative proportion of maximum probability weight per each molecular subset interval. \( \lambda_1 \) and \( \lambda_2 \) are constant coefficients for the fine adjustment of the slider weight chain to work efficiently (see Chapter 5 and appendix 5).

'Slider I' interface provides access to various simple scission models and the platform to create a wide variety of permutations and combinations of scission events by means of setting weighted probabilities to each of these. The design restricts the occurrence and extent of individual events according to their set percentage and rank order. The latter strategy thus can be enforced to vary at each of the outer time-cycles that represents a time slice of the given total decay time. 'Slider II' interface functions in similar ways, which act on the extent of participation of each of the structural subsets of the entire polymer populations. Thus this interface helps to create reaction variation according to structural differences and configurations of the latter. The 'Data-entry' dialogue box interface provides for creating variations in the minor attributes such as 'Weak-link' intervals, 'CutLength' and 'CutPercent' fragment sizes, percent 'Unzip', inner time-cycle length, percent interference etc. The above composes a computer aided iterative model creating a Monte Carlo dynamic approach.
8.4.3. Introduction of Non-iterative Methods

In Chapter 5 a transition from the iterative method of calculation of MWD to a non-iterative method is described to avoid the disadvantages of iterative means of calculation and to introduce different approaches to model complex scissions. One can cut down the long span of thousands of iterations each of which only mimic single scission per each unit time scale. Despite the popularity of Monte Carlo iterative method in areas of general polymer chemistry simulation, the method is very time-consuming and lacks reproducibility. The treatment can be reduced to an instant calculation of MWD yet still maintaining the same probability regime throughout the total decay process and successfully reproduce the different trends of molecular distribution curves in less time. Two such novel methods with a more direct approach to defining complex reactor molecular dynamics have been achieved in the current project work to show their potential for future further modifications:

(a) Algebraic exact statistic method
(b) Markov probability matrix method

All three models – the iterative Slider and the above two mathematical models are statistically equivalent but mainly differ in their approach to the MWD calculation of the various decay states of a polymer substrate. The algebraic exact statistical method calculates the new generation of scission fragments that are evolved at every decay phase in terms of expected exact probable outcomes taking into account the variability of the chain sizes and structural differences for each outer time cycle. The Markov matrix model, on the other hand, determines this calculation by means of multiplication of matrices for a number of unit times (hours in the case of cellulose-like polymer decay), where the primary matrix must be a square with equal size of vertical and horizontal array dimensions. The matrix contains a desired number of transition probabilities that provide the scope to enter preferential and variable rates, based on the different categories of molecular subsets.
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This produces a history independent molecular weight distribution for a preset time.

8.4.3.1. Introduction of Markov Statistics

The application of the above method is very rare in the case of polymer depolymerisation. Only one such application was found in the literature (Huang et al., 1995). However, Lowry, G.G. (1970), showed how to obtain a Markov chain transition probability matrix to calculate PCLD for a stepwise polymerisation (described in Chapter 5). This concept was taken in an attempt to portray cellulose depolymerisation as an example. The following new master equation was successfully deduced to suit the properties of cellulose decay. This further presents an example of the application of a non-iterative or instant method of calculating temporal MWD. The following set of equations calculate the concentrations of each category of molecular subsets, where their distribution, which changes with time $t_1$, $t_2$, $t_3$, $t_4$ ............ $t_n$, was considered as a Markov process. Thus if the chain distribution is known at a certain hour the same could be predicted and calculated for the next subsequent hours by means of a series of matrix multiplications as follows.

\[
\prod_i = \prod_0 P^i \quad \text{where} \quad \prod_i \text{ refers to } M \times 1 \text{ matrix of proportion of certain chain-lengths at } i^{th} \text{ hour, } i=0,1,2 \ldots \ldots m \text{ and } P \text{ is a } M \times M \text{ matrix consisting of probabilities of rate of transitions between the transient states defining the transition of high molecular weight species into those of a low molecular weight category.}
\]

\[
\prod_1 = \prod_0 P^1
\]

\[
\prod_2 = \prod_0 P^2
\]

\[
\prod_3 = \prod_0 P^3
\]

\vdots
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\[ \Pi_m = \prod_i P_i \]

\[ \Pi_m \Rightarrow \text{Yields the desired polymer chain-size concentration at } m^{th} \text{ time of the decay process required to construct the polymer chain-length or MW distribution. The former can be obtained by solving equation (26) through the set of equations starting from (28) to (29) for } m \text{ time steps.} \]

However the application of the above involved difficulty in constructing as these required the initial zero and 1 hour concentrations for the ease of constructing the unknown transition probability matrix \( P \). Specially in the case of cellulose, as the lab-experimental data were obtained at irregular time intervals. This would normally require repeating the matrix multiplication for a large number of times in order to solve the set of equations to obtain desired transition probabilities. This situation was avoided by using an interpolation method - Newton's divided difference formula. The use of the latter made it much easier to solve the above problem and helped to get the closest possible values for a particular time MWD curve data set using the lab-experimental data as known parameters. The transition probabilities of the molecular subset rates for the starting matrix were then deduced on the basis of the following set of regression equations, sampling any two \( x_i \) from the corresponding \( i^{th} \) subset.

\[ \beta(x) = \frac{1}{n} \sum \frac{(t_i - \bar{t})(y_i - \bar{y})}{\left(\bar{t} - \bar{t}\right)^2} \]

\[ \alpha(x) = \bar{y} - \beta(x) \bar{t} \]

where

\[ y_i = \alpha(x_i) + \beta(x_i)t_i \]

\( x_i \) = chain length, \( t \) = time-unit, \( y_i = f(x_i, t) \) (frequencies at \( \log(x_i) \)), \( i \) = length index.

(details in Chapter 5)
sampling of $x_i$: Choose two $x_i$'s from each of 6 subsets from the whole polymer chain population namely the longest length subsets to the smallest length subsets in descending order of chain-length. Their corresponding $y_i$'s denoting the frequencies were then determined from the above equations on the basis of sampling from the experimental data starting from zero time distribution to the final time distribution which are gradually changed due to partial degradation of longer chain sizes into two shorter lengths with the progress of time (in hours).

8.4.3.2. Introduction of Algebraic Exact Statistics

The preliminary concept was based on a simple algebraic mathematical induction method where probability outcome $P_{k,n}$ for a chain length $k$ implies $P_{k+1,n}$, where $k \geq 1$ for all $k$, referring to a polymer chain-size and $n$ referring to an unit time-cycle from the total time of molecular decay. $P(k,n)$ represents the probability function of a chain scission event for time-cycle $n$, which can be represented in the following polynomial of degree 2,

$$
= X_{k,n} + \frac{1}{T_n} \left[ (X_{2k+1,n})^2 + 2 \cdot (X_{2k,n})^2 + (X_{2k-1,n})^2 - (X_{k,n})^2 \right]
$$

The following proves total probability $= 1$ for $N$ number of polydisperse chain lengths, where the probability of a bond cleavage per each type of chain is weighted according to its frequency and $T_n$ is the total sum of probabilities for a time-cycle $n$.

$$
\sum_{k=1}^{N} \frac{P_{k,n}}{T_n} = \sum_{k=1}^{N} X_{k,n} = \frac{T_n}{T_n} = 1
$$

Further development of the above concept provided a discrete model to cover all different cases of simple chain scission mechanisms, which were
further modified to semi-continuous and finally to a continuous form. This is briefly narrated below (details given in Chapter 5 and Appendix 5).

**Discrete model**

It was assumed that precisely one bond is broken at each step. This implies that only polymers of length 2 or more are picked at each step since monomers do not have any bonds that can be broken. Let \( d(n,t) \) = number of molecules of length \( n \) at time \( t \). Then the total number of molecules at time \( t \) is worked out as, \( N = \text{length of the longest molecule} \).

\[
T(t) = \sum_{n=1}^{N} d(n,t)
\]

The following probability was structured on the assumption that molecules with the largest frequency would be most likely to degrade. The probability of rate of reactivity of a molecule of length \( n \) at time \( t \) is

\[
P(n,t) = \frac{d(n,t)}{T(t) - d(1,t)}, \quad 2 \leq n \leq N,
\]

(ignoring monomers). Where

\[
\sum_{n=2}^{N} P(n,t) = 1 ...............................................(1)
\]

The general version of this method uses the following master equation

\[
d(n,t+1) = \sum_{k=2}^{n-1} P(k,t) d(n,t) + P(n,t) [d(n,t) - 1]
+ P(2n,t) \left[ \frac{1}{2n-1} (d(n,t) + 2) + \frac{2n-2}{2n-1} d(n,t) \right]
+ \sum_{k=n+1, k \neq 2n}^{N} P(k,t) \left[ \frac{2}{k-1} (d(n,t)+1) + \frac{k-3}{k-1} d(n,t) \right] ..................(2)
\]

The above is a general theory of the model for a random scission process. This can be modified to derive other specific scission model derivatives such as ‘Cut in half’, ‘Cut Fixed Percent’, ‘Cut fixed Length’ and ‘Unzip’. The theorem and proof for each is included in the Appendix 5 (section 5.4.1.1.3).
Transformation to a Continuous Model

The preliminary application of this method was on a semi-iterative basis by using the Delta correction formula (see chapter 5 section 5.4.1.1.2.). The following equation was derived for MWD calculation of a chain-length \( k(2 < n < N) \) for the time period between \((t, t + \delta)\) in the case of 'Cut in half' scission model (considered the easiest of all),

\[
X_{n-\delta} = X_n - P_{n-1} \delta + 2 \cdot P_{n-1} \delta + P_{n-1} \delta + P_{n-1} \delta, \text{ where } 1 < \delta < \varepsilon, 2 < n < N
\]

This can be implemented in the general equation,

\[
d(k, t+\delta) = d(k, t) + \delta \left( -P(k, t) + \sum_{k=n+1}^{N} \frac{2P(k, t)}{k-1} \right), \text{ where } 1 < \delta < \varepsilon, 2 < n < N \ldots \ldots (4)
\]

\( \varepsilon \) refers to a finite upper boundary. However, simulation experiments showed that increasing the length of these stationary time segments \( \delta \) degraded the integrity of the MWD curvature to some extent. The smaller the magnitude of \( \varepsilon \) the less is the significance of the latter. However, equation (4) presents a derivative of the function \( d(k, t) \) over time step \( \delta \) by Euler's method as follows,

\[
y(t+h) = y(t) + hf(t, y) \text{ where } h \to \varepsilon \ldots \ldots \ldots \ldots \ldots (5)
\]

In place of very infinitesimally time increments \( \varepsilon \), in (4) \( h \) is incremented by a series of finite time steps \( \delta \) that can be considered very small when compared to the large magnitude of total decay time. Thus equation (4) can be written in the above differential equivalent of equation (5),

\[
\lim_{h \to \delta} \frac{d}{dt} d(k, t+h) = - \frac{N}{\sum_{n=1}^{N} d(n, t)-d(1, t)} d(k, t) + h \left( \sum_{k=n+1}^{N} \frac{2}{k-1} \frac{d(k, t)}{\sum_{n=1}^{N} d(n, t)-d(1, t)} \right) \ldots \ldots (6)
\]
The equation (6) can be solved more accurately using a popular numerical method Runge Kutta. A vector of \( d_i \)'s and \( K_i \)'s can be derived for each chain length from the time sequential derivatives of the general form,

\[
y(t_{i+1}) = y(t_i) + hf(t_i, y(t_i)) \quad \text{where} \quad K_i = hf(t_i, y(t_i)) \quad \text{.........(7)}
\]

\( y(t_i) \)'s representing \( d_i \)'s can be derived by the above method for a number of equal increments of \( h \) for a better prediction of the change in outcomes of the entire process trajectory from \( t_i \rightarrow t_{i+1} \). This is a very elaborate procedure, which is left for future research.

The continuous form of this model is presented in the following equation.

\[
\begin{align*}
\int_{t=0}^{t=\delta} &\int_{k=S_0}^{k=S_0} d(k,t+\delta) \quad dk \quad dt = + \int_{t=0}^{t=\delta} \lambda_1 \left( \int_{k=S_0}^{k=S_1} d(k,t) \quad dk \right) \left[ P(\phi,t) + \int_{k=S_0}^{k=S_1} \frac{2P(\phi,t)}{k-1} \quad dk \right] \quad dt + \\
&+ \int_{t=0}^{t=\delta} \lambda_2 \left( \int_{k=S_1}^{k=S_2} d(k,t) \quad dk \right) \left[ P(\phi,t) + \int_{k=S_1}^{k=S_2} \frac{2P(\phi,t)}{k-1} \quad dk \right] \quad dt + \\
&+ \int_{t=0}^{t=\delta} \lambda_3 \left( \int_{k=S_2}^{k=S_3} d(k,t) \quad dk \right) \left[ P(\phi,t) + \int_{k=S_2}^{k=S_3} \frac{2P(\phi,t)}{k-1} \quad dk \right] \quad dt + \ldots \quad (8)
\end{align*}
\]

\( P(\phi,t) \Rightarrow \) a function of \( \phi \) and \( t \) (a time segment of total time).
\( \phi \Rightarrow g(R_s, t) \Rightarrow \) a rate distribution function of the chain length subsets range \((S_n - S_{n-1})\), which is assumed to be constant for a small time segment \( dt \). \( \lambda_n \quad (n = 1,2,3, \ldots) \) are probability rate coefficients for finer adjustments of the equation, which may vary among the subset intervals and in between the consecutive time segments, but in general assumed as non-variable within the extent of a time segment. Life span of partial time intervals \( t \quad (0 \rightarrow \delta) \) should be \((t_i \rightarrow \delta_i)\) indicating \( i^{th} \) start point for each successive time segment \( \delta_i \), which can vary too (see equation 9).
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\( P(\phi, t) \) refers to probability term allocated distinguishing the potential of reactivity for each molecular subset category within the range \((S_n - S_{n-1})\) that remains constant for a period of \( \delta_i \). \( \phi \) can be determined from the nature of decay rates of the polydisperse polymer subsets graded by their different sizes as observed from laboratory experimental data, assuming these rates vary with time and also with temperature and the atmospheric condition of the decay.

8.5. Modelling of Real Time

Three non-linear time models have been investigated. The first one is based on Emsley-Heywood pseudo first order kinetic model that was derived from lab-experimental data describing cellulose kinetics. The other two models were formulated to provide alternative means that might be useful for other polymers and for further future investigation. The concepts of these models are briefly presented below.

8.5.1. Exponential Distribution (time model 1)

The following non-linear equation (Emsley and Heywood, 2000) was used to represent exponential time distribution, suited to cellulose decay kinetics.

\[
\frac{1}{DP_i} - \frac{1}{DP_0} = \frac{k_1}{k_2} \left[ -e^{b_i} \right] \quad (34)
\]

Where \( k_1 = \text{the initial bond-breaking rate}, k_2 = \text{the rate constant at which } k_1 \text{ changes.} \) The above time model is mostly used in the simulation of cellulose molecular degradation kinetics.
8.5.2. Poisson Distribution (time model 2)

If the overall nature of the number of bond disintegrations for a particular time interval \((0, t)\) is considered as random, then the number of bond-breakings in the subsequent time series can be shown to follow the classical Poisson distribution. Considering \(k\) cases of events' occurrences, in time intervals \(t\) and \(\Delta t\) are independent of each other, the total conjugate probability becomes,

\[
P_{t+\Delta t}(X = k) = \sum_{j=0}^{k} \left( P_t(X = j) \ast P_t(X = k-j) \right) \ldots \ldots \ldots \ldots (50)
\]

Comparing with radioactive disintegration (Yankovsky, G., 1969), this method of time evolution can be interpreted in the following form of differential equation,

\[
\frac{dP_t(X=k)}{dt} = -m^*P_t(X=k) + m^*P_t(X=k-1) \ldots \ldots \ldots (58)
\]

The solution of the above equation yields the following.

\[
P_t(X=k) = e^{-mt}(\frac{mt}{k!})^k \text{ for } k \geq 0 \ldots \ldots \ldots (65)
\]

Where for a particular time period, \(t\) and \(m\) are constant.

The above is applied in the case of cellulose, relating unbroken bonds to time (presented as inner time cycles, \(t(n)\)) in an exponential manner.

\[
d(n) = ae^{-bt(n)} \ldots \ldots \ldots (66)
\]

Where \(a, b\) are constants, \(d(n) = \) unbroken bonds remaining of the total / average chain-length population after \(n\)th time slice \((n=1,2,3,\ldots)\)

\(t(n) = t_1 + t_2 + t_3 + t_4 + \ldots \ldots + t_n\), = Number of inner cycles after \(n\)th time slice.
8.5.3. Rectangular Hyperbolic Distribution (time model 3)

A parametric function of similar form to one branch of a rectangular hyperbola in the first quadrant of the coordinate axis was constructed from the second order rate equation as below.

\[
y = \frac{1}{k_1 t + k_2} \tag{77}
\]

Where \(k_1\) and \(k_2\) can be regarded as rate constants. \(k_1\) represents the main resultant rate constant and \(k_2\) is a co-efficient that is worked out from the initial conditions of the polymer (e.g. initial total bonds) and determines the rate curve vector in relation to the total time of decay. The medium and long chains are assumed as the main component participants in the molecular decomposition. Their molar concentration is worked out from the above equation in terms of undegraded bonds remained at the end of a decay cycle. \(k_1\) is calculated from the equation (22) and (23) of section 5.4.2.2. The resultant reaction rate shows a close approximation to a second order kinetic equation and as such the initial increase in rate depends on the square of the initial concentration of the average DP. On reaching a limiting DP the decline in rate becomes infinitesimal. The rate curve by this means thus can provide an alternative to simulate cellulose-like or synthetic polymers, where rate cannot be described by simple first order kinetics.

8.6. Kinetic Parameters from Simulation Models

- The simulation experiments show that the time progression of degradation and its kinetic behaviour can only be truly monitored from the number of bonds breaking per unit time or per each reaction extent. In this respect, a well-defined scheme of distribution of time subsets is required that depends on the characteristics of the reactor as well as the polymer system.
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- The time model 1 is primarily used in this thesis as cellulose substrate was chosen as a suitable polymer for the present degradative investigation by means of simulation modelling.
- This model is directly based on the kinetic equation (34) derived from the lab-experimental tests that simulated accelerated conditions for the electrical transformer where cellulose is used as insulator.
- However, the above equation has limitations. It was found to be only valid for certain range of DP values, beyond which the equation exponents become infinite or inconsistent. This may be due to values for DP were calculated in different manner in lab test to simulation experiment. Lab-test calculates DP using Mark Houwink relationship on the basis of intrinsic viscosity, read from the viscometer directly. In simulation this was not possible and so DP was calculated as first moment.
- However, in both cases DP values being discrete integers can have large differences between subsequent time series that may vary to a great extent. The latter was found to be difficult to compensate for and as such made the time values inconsistent in some cases of simulation sampling.
- In order to avoid the above problem other statistical time distribution methods such as classical Poisson (time model 2) and random Geometric (time model 4) were investigated. In addition to these two alternative approaches, a derivative of a Rectangular Hyperbolic function (time model 3) was deduced to evaluate subsets of time interval that would produce more consistent rate curve pertinent to the cellulose kinetics.
- In order to incorporate the very exponential nature of cellulose disintegration kinetics time model 3 was found most suitable. Unlike time model 1, time models 2 and 3 are designed to calculate time not on the basis of DP but on the basis of the number of remaining undegraded bonds at the end of each degradation time cycle. These options were found to have the potential to yield more sensitive and reliable results than model 1 that is limited to accept DP values for time calculation.
- Use of number of undegraded bonds, which is a real number, the above problem was possible to eliminate. However, this would not provide the rate constants $k_1$ and $k_2$ for cellulose kinetic profile, which would be
available using time model 1. Hence in order to avoid any further problems or side effects to deal with for which there was not enough time in the current project, a compromise was reached. For most part of simulation, time model 1 is used and only where any invalidity was faced time model 2 or 3 were used.

- However concepts of time distribution models such as 2, 3 and 4, as alternatives to time model 1 for simulation of real degradation time, are introduced in this thesis. These methods can be hoped to have potential application to suit the other polymer degradation characteristics. This could constitute future project investigation using other polymer as subject of research study.

- The kinetic parameters from the Arrhenius equation parameters i.e. activation energy ($E$) and pre-exponential ($A$) were obtained from the different simulation models using time model 1 and 2 and were compared with those from lab-experiment of cellulose-accelerated tests. The both sets were found to be in reasonable agreement with the latter, but further work is required to improve the correlations.

- A good agreement between the simulation and observed kinetic results were also reached for the degradation cases where the proportions of degrading agents were varied. The latter are found to be the key degrading agents in electrical transformer reactor system.

### 8.7. Estimation of Polymer Durability

Chapter 6 presents the simulation experimentation results in relation to derive temporal changes in MWD curves, the related moments and other moment-derived parameters for different temperatures. The mathematical models (described in chapter 5) were used to derive the results. The simulation program in this project has been shown to be a useful complementary technique to lab-experiments for investigation of polymer molecular dynamics in the following main aspects.
to identify the probable molecular events that take place in a complex degradation process with the rise of temperatures and in different environments.

to establish the trend of temporal changes in MWD curves in different environmental conditions.

to deduce the profile of other related attributes (e.g. moments, polydispersity index, number and weight averages etc..)

to derive a relationship between time and a range of temperatures reflecting the intensities of the decay changes by using MWD curve shifts as a measure guide. The relationship is polynomial nature and in the case of cellulose it fluctuates between square to cubic.

\[ \Delta t = C \pm 2a \left( \frac{\Delta T}{b} \right)^x \] ..........................(6.6)

\( \Delta t \) = amount of time difference due to change in thermal energy
\( \Delta T \) = magnitude of temperature difference,
\( x \) = exponent (1,2,3,...) that depends on the above deflection
\( b \) = constant, determined by the sensitivity of the equilibrium of the system to the thermal deflection,
\( a \) = co-efficient that depends on the amount of kinetic rate change due to increase in thermal energy and is related to the time elapsed between two subsequent peakshifts.
\( C \) = an arbitrary quantity used to balance any deviation from the actual experimental mean and thus act as a statistical standard deviation.

The above is used to simulate the extent of polymer (cellulose) durability or functional life in a hypothetical slow and accelerated reactor. A table of estimates is given in Chapter 6, which shows close resemblance to the predicted shelf life of cellulose by extrapolation of lab-experimental established data to lower temperatures by Emsley-Heywood, using pseudo first order kinetic equations.
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- The equation 6.6 provides time-temperature relationship and an alternative way to estimate decay progress in terms of measuring the time of MWD curve-peak shifts from HMW region toward LMW region and determining the nature of variation due to differential time-temperature variation. This helps to extrapolate the results to the temperatures of the actual reactor e.g. in case of commercial use of cellulosic materials the reactor operating temperature can be as low as 60-80°C. For example to reach the limiting DP (200-150) the highest temperature (160°C) would take 0.07 years in air and 12 years in oil, whereas operating temperature (60°C) this would be 400 years in air and 716.4 in oil. The latter is in good agreement with the predictions of Emsley and Heywood (2000). These estimations obtained from equation 6.6 for a range of temperature are given in table 2.

8.8. Inferences from Simulation Results

- Statistically tested results (refer to table 6.7 and 6.8 and Appendix 6) summarise the following.

(a) Mechanism 1 (Cutlength+Weaklink+Unzip) relating fixed length end-cut mechanism, in concert with unzipping operations of the chain fragments, appear to be more commonplace for molecular disintegration in air than in oil. In contrast mechanism 3 (Cutpercent+Weaklink+Unzip) appears to be more statistically appropriate in oil, where an end-cut of an arbitrary percentage of the polymer chain-length co-exists in synergism with unzipping actions alone or in conjunction with cutchop cleavages. The intermediate decayed MWD curve broadening effects were more pronounced in oil than in air from GPC chromatograms. The simulation results in this thesis show that the main reason for the former is partial zipping effects, which is also supported by the moment profiles as described in Chapter 6.
(b) The statistical results demonstrate that mechanism 3 is the most important scission mechanism throughout the cellulose decay process. Mechanisms 1 and/or 2 (Cutpercent+Cutlength+Cutchop) compete with 3 depending on the type of medium in which the degradation is carried out. The extent of this interference is not necessarily dependent on temperature. However, the rise in the latter increases the rate of the reactions and the entropy of the system, which may contribute to favour either mechanism 1 or 2.

- Effects of molecular mechanisms: The results obtained from the simulation experiment study with the MWD trends, obtained from different combinations of scission events indicated the following.

(a) Bi/tri modality is displayed by the MWD intermediates during the initial phase of decay by a combination of two scission mechanisms – 'Cutpercent' or 'Cutlength' and 'Weaklink'.
(b) The initial peak splits into bi/tri modal and shouldering effects disappear with the introduction of unzipping i.e. 'Cutchop' or 'Unzip' mechanisms.
(c) Tri-modality in trends 3 and 7 was identified as a pronounced effect of 'Cut-in-Half' i.e. central scission. The effect of the latter alone (i.e. not in combination with other scission modes) resulted in a multi-modal pattern, shown in Chapter 3. In this Chapter the algorithm was set on log-linear scale, which also showed trimodal patterns rather than bimodal when in combination with mixed scission modes. This mechanism has been shown to be more common in polymer chain decay affected by mechanical or stress induced mechanisms.
(d) Inclusion of more scission events (>3) in a Slider event oriented reaction composition tended to display more uniform lateral MWD curve shifts similar to the trend observed in the case of random and equivalent exposure of different molecular assemblies along the polymer matrix.
(e) Absence of 'Unzip' reaction resulted in more curve deformity and irregular indefinable shapes.
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(f) 'Cutpercent' scission reaction tends to give rise to peak broadening effects in the MWD intermediates similar to the effects of thermo hydrolysis.

(g) 'Cutlength' displayed similar effects or shouldering and as such can be identified with the effects of thermolysis or a part of auto-radical chain reactions, which are more likely to occur as the temperature rises.

(h) Occurrence of more 'Unzip' in the reaction strategy tends to minimise uncontrollable accumulation in chain sizes with the evolving generations of fragment population by its annihilating effect. This helps restore a balanced Gaussian unimodal form of the MWD curves during the end decay phase. By controlling the curve broadening, this mechanism also controls continual high increase in polydispersity.

- Effects of temperature: Experimentation with three temperatures (120°C, 140°C and 160°C) provided a good basis for comparative study. On the basis of simulation investigation of a complex macromolecular (cellulose) degradation the following inferences can be drawn.

(a) The lower the temperature the more gradual the rise and weaker links prevail during the earlier decay, superseded by 'Cutpercent' or 'Cutchop' mechanism during the mid-phase of decay. These mechanisms display the effects of hydrolytic attacks in the more ordered regions or crystalline domains of the polymer.

(b) In the case polymers of uni-helical backbone composition (e.g. cellulose, chitosan) persistent attacks on the long chain 'tie' molecules that run from the crystalline to semicrystalline regions initiate the onset of progressive decay. 'tie' chains link these two regions and hence build a bridge between the two domains.

(c) In the case of multi-helical polymers (e.g. DNA and RNA duplex and multi-stranded polysaccharides), initial deterioration occurs at the weaker links (those least shielded by of co-operative forces).

(d) In the case of branched chain or cross linked polymers (e.g. polyethylene, polypropylene) the initial attacks occurs on the most preferable end site of branching from the parent molecules.
(e) The above 3 strategies have been found more likely to be brought about by the hydrolytic or thermo hydrolytic or enzymatic action in the case of condensation polymers.

(f) The higher the temperature the more dominant is the effect of the 'Cutlength' mechanism in conjunction with 'Unzip'. Both successfully simulated a reaction strategy of thermolysis (or auto catalysis).

(g) Bond scission rates and percent profile both between cycles and compared from the initial bond total were consistent with each other and between the three temperatures and three rates (i.e. per second, per minute, per hour). In creasing temperature increases both reaction rates and percent mobilisation, increasing approximately 20 times with every $20^0$C rise.

(h) While more fluctuation of rates between the time-cycles was visible compared to the smooth rise in total bond turnover, the variations can be accounted for in the random nature of the Slider model. This also explains the reason for slight inconsistency between the smallest (e.g. per min) unit time rate profiles and their largest counterpart (e.g. per hour). This is more significant at $140^0$C.

(i) This variation among the number of bond scission trends may be justified in terms of the differences in the direction, amount and speed of configurational disruption and changes those are experienced first and foremost by the constituent molecular assemblies. Availability of thermal quanta and vibrational energy is responsible for bringing about these disruptions among the helical configuration in the solid-state polymers. Thus certain scission mechanisms with a lower thermo-dynamic demand can get preference over those with a higher demand, but the latter reaction can gain more dominance with rise of temperature. Thus for example a combination of 'Weaklink' and 'Cutpercent' has been found more preferable in the lowest temperature (i.e. $120^0$C) whereas 'Cutlength' and 'Unzip' were found to take precedence at highest temperature (i.e. $160^0$C). A competition between these two extreme strategies was observed to account for the deformities observed at $120^0$C.
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Effects of environment: The effects of varying the surrounding environment of the reactor and the nature and progression of decay was examined by simulation experiment. In this way a more exhaustive study than can be made than is possible from a lab based experiment. Simulation of environmental changes such as reaction medium (e.g. air, oil and vacuum) and proportion of degradative catalysts (e.g. oxygen, moisture, temperature) was effected in the respective experiment by means of program interface driven function commands and the resultant graphical profiles were examined. Important inferences drawn are given below.

(a) The differences in reaction medium (air and oil) influence profoundly the individual reaction kinetics and hence rates among the different reactive structural components (subsets) of the polymer.
(b) The most significant invasion in the HMW regions is achieved at the highest temperature (i.e. 160°C), and is more clearly exhibited in oil than in air.
(c) Semi-crystalline regions (subsets 3 and 4) seemed to be most affected at 140°C in both oil and air.
(d) The invasion of ordered or semi-ordered (i.e. HMW and MMW) regions was less profound at 120°C in oil than air and rapidly tailed off.
(e) The above showed that hydrolytic reactions are less likely to persist into the moderately advanced phase of decay in oil at lower than they are at higher temperatures and least so in air.
(f) In contrast oxidative or thermal autocatalysis seemed to dominate in air more than in oil and also was promoted by the rise in temperature in both media.
(g) The lower middle chain subset is most affected by decrease of temperature and the higher middle chain subsets are least affected.
(h) Simulated DP and Q profiles were obtained from simulation MWD experimental samples, where the proportions of degrading agents
e.g. oxygen, moisture and temperature were varied. Antagonistic interactions between water and oxygen at low water and temperature levels were reproduced. A strong synergism between water and temperature but a weaker synergism between oxygen and temperature as observed in lab experiment was also shown.

(i) An estimation of the main scission mechanisms obtained from the simulation experiments at different temperatures and different stages of decay are given in table 1.

**Comparison of the outcome from Slider, Markov and Algebraic Exact mathematical models:**

Markov calculations are based on transition probability matrices where the required parameters can be derived from prior obtained lab-experimental kinetic data. Thus it allows a more stable form of results with regard to the simulation of the decayed states of MWD curve intermediates and has the potential mimic the detailed curve deformities and shape changes from the intact initial structure. In contrast, Slider model calculations are based on an overall stochastic iterative event oriented schemes that are designed to calculate changes in the molecular trajectories for each unit time cycle in a stepwise manner. This makes the resultant calculation more randomised and less reproducible. The very random nature of the algorithm caused significant fluctuation in bond mobilisation from cycle to cycle. Thus despite the tremendous scope for flexibility, the results are the less reproducible than those of the Markov and maths models.

The algebraic maths model falls in between the two extremes of stability and reproducibility. It has the potential to yield consistent outcomes and errorless results from the same sample simulation experimental conditions and the repeated model-runs. This model demands the predictable nature of reactions or structural and environmental implications to be set out in a number of definite rules. These can then be incorporated in algebraic and statistical formulae defining the whole system. This approach may impose some inflexibility towards randomisation but alternatively may render more
control over the characteristics of the system to be simulated. However, the reproducibility depends to some extent on $\delta$ value distinguishing the duration of inner time intervals. The latter parameter forces the discrete model to transform into a more continuous form that needs to make assumptions about the probability density distribution for the scission of different chain categories, which must remain constant for the time-period $\delta$. This may result in loss of fine detail from the simulated MWD curves. Further future work is required to investigate the potential of these semi-continuous and continuous models, which offer more direct approaches similar to Markov statistics. They concepts presented here do however provide a good basis for future exploration of the application of instant methods of calculating MWD in the areas of both polydisperse and monodisperse polymers as well as in the cases of polymer synthesis or degradation.

All three models presented in this thesis provide a suitable and reliable scheme for intermediate MWD calculation for both complex or simple reactor systems. Each of these new methods and concepts of time distribution provides opportunities for further mathematical research in the area of commercial polymer kinetics and durability studies.

### 8.9. Suggestion for Future Work

The transformation to instant calculation requires further work and enhancement. This directs future opportunity for extending simulation research of polymer degradation or synthesis into more mathematical areas of research. The probabilistic and higher mathematical and statistical algorithms developed in this project can be explored in the areas of polymer synthesis too as well as other polymer behaviour study - in general with a little modification.

Improved performance of the 'polydeg' program could be achieved by introducing multi-tasking or multi-threading facilities and code structure could have been altered accordingly with more time. The unavailability of the second option is due to the original skeleton format was in SDI (i.e.
single Document interface) format. This also restricts to some extent the multiple window view facilities. To avoid this disadvantage the program needs to be restructured from the very beginning into MDI (i.e. multiple Document interface) and MT (multi-threading) format so that each separate simulation experiment can have their own document and separate view provisions including separate thread processor linking arrangement in order to cut down a long job queue and waiting time for a processor to be free. But this format change will impose re-writing the entire program modules and code.

The other alternative is the first option – it may be possible to make the present program multi-processing by using the UNIX operating system in addition to Windows, possibly in a client server configuration. The UNIX system is naturally multi-tasking and if the degradation processing can be run in UNIX following the data input job and their storing into appropriate variables including some of the message and command passing necessary to reach the simulation experimental model-run stage. This way processing time can be further cut down to a great extent and do not need to rely on 1 Giga-Hz or above Intel processor to achieve faster processing.
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