Improved Methods for the Thermal Analysis of Cure in Polymer Composites

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Abstract

Measurement of the degree of cure of composite materials is vital to both research and manufacture of these materials. The glass transition temperature ($T_g$) is a measurable material property that can be used as an indicator of the degree of cure. The three most common thermal analysis techniques used to measure $T_g$ are DMA, TMA and DSC (i.e. dynamic mechanical analysis, thermomechanical analysis and differential scanning calorimetry). There is a current need to improve the experimental methods and analysis of data when using these techniques, where issues such as thermal lag can negatively impact data precision. In this work, a method using multiple tests at different heating rates has been applied to these three techniques to eliminate the effect of thermal lag as well as assess other variables that can influence test data; specimen moisture condition, specimen thickness and fibre type. It was shown that while thermal lag can be accounted for, there are remaining slight differences between DMA, TMA and DSC $T_g$ data, which can be expected due to the different response modes involved (e.g. mechanical, thermal expansion, calorimetric). For DMA testing, a simple relationship has been proposed, relating heating rate and specimen thickness, which can account for the effect of thermal lag when comparing data obtained for specimens of different thicknesses or for the same thickness at different heating rates; the relationship is supported by relevant experimental evidence.

It was shown for materials with different degrees of cure that the relationship between $T_g$ and degree of cure followed the same trend regardless of differences in $T_g$ measured by the three techniques. Preliminary experiments indicated that FTIR showed promise for measurement of the degree of cure of composite materials, in addition to measurements by DSC.
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1 Introduction

1.1 Background

The UK composite materials industry is currently valued at £12.3bn, with a predicted growth to £20bn by 2030 (1). As the world advances, two of the greatest motivators in science and technology are the longstanding drive for advancement through ever-increasing performance, and the current need for preservation, where there is a growing focus on sustainability and reduced carbon emissions. Composite materials have the potential to meet demands in both of these areas, where interest in composite materials is largely centred on their ability to facilitate lighter-weight modes of transport, reducing fuel consumption and thus enabling a reduction in carbon emissions, as well as delivering increased performance in many other sectors. These sectors include rail, oil and gas, renewable energy, marine, aerospace and automotive, competitive sports, infrastructure and smart materials.

Composite materials are composed of two or more materials, specifically chosen and tailor-made to have better properties than those of their constituent parts. In the case of polymer matrix composites, the materials are designed to capitalise on the light weight of the polymer matrix and the strength of the reinforcement. In addition to weight-reduction, polymer matrix composites can be designed to possess properties such as flame-retardance and corrosion resistance where traditional materials can often fall short. Advancing the cost-effectiveness and reliability the manufacturing processes for composite materials is crucial for current users as well as future uptake of these materials.

In the manufacture of polymer matrix composites (PMCs), a liquid resin is distributed through the reinforcing fibres and subsequently cured to form the solid matrix required to achieve the desired material properties. Obtaining a fully cured matrix is crucial in order to obtain the full performance, especially under environmental exposure. Thermal analysis techniques have long been used to support the manufacturing process through measurement of the changes which occur during the resin cure process and assessment of the state of cure itself. Thermal analysis, used in both industry and academia, encompasses a wide range of materials
characterisation techniques which measure changes in material properties when subjected to a known temperature profile in a controlled environment. Thermal analysis measurement is used to support R&D, to communicate material capabilities, for contractual specifications and quality control.

One of the key measurable thermal properties of composite materials is the glass transition temperature, $T_g$, which not only provides information on the maximum service temperature of materials, but can be used as an indicator of the degree of cure of composites. Measurements of the glass transition temperature can vary greatly between different thermal analysis techniques and data analysis methods and is often dependent upon the heating rate used in testing.

In addition to measurement of the $T_g$, cure monitoring technology is a growing focus of composite materials research. Cure monitoring encompasses measurement technologies with the capability to provide live feedback on the state of cure of a PMC during manufacture. The effective integration of such technologies will enable a reduction in cure times and temperatures, which are currently conservative, as well as embedding quality during manufacture. The successful realisation of the proposed cure monitoring technologies will be facilitated by data obtained from existing thermal analysis techniques used for validation, including dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC).

It follows that the precision of these thermal analysis measurements is necessary to enable uptake of composite materials by informing standards and allowing the full potential of the material properties to be realised. Precision measurement or precision data is defined as data which is both repeatable (by the operator) and reproducible (by other users) to a specified degree of accuracy. The main drivers for improving test methods are summarised in Figure 1.1, which shows that measurement precision of thermal analysis techniques impact all areas of composite materials manufacture, from research and development through to ensuring the quality of the finished product. Developing an understanding of the degree of certainty with which these measurements can be trusted and continually improving test methods will underpin the development of new cure monitoring techniques as well as composite materials technology overall. Finally, measurement
science can assist publication of new standards and regulations which are necessary for the uptake of composite materials technologies.

![Figure 1.1 – Drivers for improving the thermal analysis test methods used in the composite materials industry](image)

1.2 Project Aims

The aims of this work are to improve upon the thermal analysis methods used to measure the glass transition temperature by addressing the issues which affect precision and communication of measurements of this important material property. The measurement of the glass transition temperature as a useful means of assessing the degree of cure of composite materials will also be studied. The overall aim will be to provide guidance on the best methods for the thermal analysis measurement of $T_g$ as an indicator of the degree of cure.

1.3 Thesis Outline

In this Chapter the importance of relevant and accurate measurement science as a means to underpin advancements in composite materials technologies has been highlighted. The next chapter will include scientific background of polymer cure and
a review of both cure monitoring technologies and thermal analysis techniques. This is followed by a detailed description of the experimental methods and material preparation in Chapter 3.

In Chapter 4 an assessment of some of the variables that can influence the value of $T_g$ measurement by DMA have been studied. These include the effects of specimen conditioning, i.e. drying, the influence of the type of fibre used, the effect of specimen thickness on thermal lag and modelling of the heat transfer through composite materials. This is followed by Chapter 5 which presents a study on TMA and DSC as alternative methods for the measurement of $T_g$. Chapter 6 summarises the previous two chapters with a discussion comparing the three techniques (DMA, TMA and DSC).

In Chapter 7 the relationship between $T_g$ and the degree of cure is studied. In addition, a preliminary assessment of FTIR as a means of measuring the degree of cure has been carried out.

Conclusions and recommendations for future work are presented in Chapter 8.
2 Literature Review

2.1 Introduction

The manufacture of polymer matrix composites begins with a liquid resin into which the fibres are embedded. The material is then cured to the solid state in order to achieve full material properties. The degree of cure is an important parameter for the development and manufacture of composites, therefore this chapter begins with an introduction to the scientific background of polymer cure. This is followed by a survey of the existing research into measurement of the degree of cure, including online cure monitoring techniques, to set the context of the state of the art in cure measurement techniques. The T_g as an indicator of degree of cure is then described and finally a review of the three most popular methods for measurement of the T_g are then discussed, along with their limitations with respect to obtaining precision data.

2.2 Background: cure of epoxy and polyester resins

2.2.1 Introduction

A number of resin systems are used in the manufacture of PMCs, including epoxy, polyester, polyether ether ketone (PEEK), vinyl ester and polypropylene. The work in this dissertation focuses on fibre reinforced thermosetting polymers, where the two most frequently used thermoset resin systems in engineering composites are polyester and epoxy. While research into the use of thermoplastics as a matrix material is increasing, epoxy and polyester remain the two most common choices based on thermosetting resins for PMC manufacture. Thermosetting polymers vary from their counterparts, thermoplastics, in that the cure reaction is irreversible and they cannot be melted, re-softened or reshaped on heating. This is as a result of the covalently bonded cross-linked structure which is formed upon curing. In thermoplastics, below T_g the polymer chains are cross-linked by Van der Waals forces, which become ineffective with increasing temperature, resulting in liquid
melt. As a result, thermosetting polymers offer greater thermal and dimensional stability than most thermoplastics and are therefore well suited to use in composite materials, where the thermal performance of PMCs is directly related to that of the polymer matrix.

2.2.2 Epoxy resin chemistry

Epoxies are a class of polymer containing the reactive oxirane chemical group, otherwise referred to as the epoxy functional group, pictured in Figure 2.1. Epoxies are widely used in high performance composites due to their low shrinkage, low corrosion, high chemical resistance, and high strength.

The formation of a cured epoxy is a two-step process. The first stage in creating a cured epoxy is the preparation of the epoxy resin, or prepolymer, which has not been fully reacted. The most common epoxy resin prepolymer used in industry today is formed from the reaction of bisphenol-A and epichlorohydrin, shown in Figure 2.2, in which the end product contains the oxirane group.

These epoxy resins are cross-linked either in a catalytic homopolymerisation reaction or through the use of co-reactants. During the curing reaction, the liquid resin reacts at the oxirane site to form the solid thermoset. A number of cross-linking (curing) agents are available for use with epoxy resins, with the most popular being polyamines, anhydrides, polyamides and catalytic curing agents (which do not act directly as cross-linking agents). In the epoxy cure reaction, the speed of cure is controlled by the type of reactant used as well as cure temperature. In the most common cure reaction, addition reaction using an amine as a hardener, two epoxy groups bond to one amine group, shown in Figure 2.3. This is the basis for the formation of the final 3D network in Figure 2.4. As the curing process uses a co-
reactant, the appropriate amount of hardener must be used to ensure full reaction. One of the associated complications during manufacturing of epoxy resins is the difficulty resulting from the need for precise measurement of the ratio between resin and hardener in order to achieve full cure and fully realised material properties.

Figure 2.2: Reaction between bisphenol A and epichlorohydrin to form epoxy resin (prepolymer)

Figure 2.3: Cure reaction of epoxy resin with amine hardener
2.2.3 Polyester resin chemistry

Polyester resins offer a lower performance but much cheaper alternative to epoxy resins. Reinforced polyester resin composites are particularly popular for use in the marine industry (boat manufacture), mainly due to their cost to performance ratio.

Polyesters can exist both as thermoplastics and thermosets. This section will focus on thermoset polyester resins. Polyester resins are most commonly formed through the condensation reaction between a dibasic organic acid and a dihydric alcohol, which forms water and the ester group from which the material derives its name, shown below in Figure 2.5.

![Figure 2.4: Cross-linked epoxy (3)](image)

![Figure 2.5: Ester chemical group](image)

When referring to a polyester matrix in the context of composites, they are generally unsaturated polyester resins such as the one pictured in Figure 2.6. To produce a cured polymer, the resin will typically be dissolved in a monomer, normally styrene,
which copolymerises with the polyester and forms the cross-links that build the 3D network of the final cured structure. The choice of monomer enables greater design flexibility for the performance of polyesters, where different monomers produce cured polyesters with different material properties. While varying the components enables the synthesis of a multitude of polyesters, the two most popular polyester resin systems used in industry are orthophthalic, which is the original polyester resin system, and isophthalic, which offers improved mechanical and thermal performance as well as improved resistance to corrosion and water ingress.

![Idealised isophthalic polyester](image)

**Figure 2.6: Idealised isophthalic polyester (4). The C=C double bond is the “unsaturated” part**

As with epoxy, resin cure is activated by a catalyst, such as methyl ethyl ketone peroxide or benzoyl peroxide. These initiators work by producing free radicals which attack the carbon-carbon double bond, reducing it to a single bond by bonding with one of the carbons, and leaving a single bond with a free radical which, in turn, reacts in the same way with other carbon-carbon double bonds on the styrene monomer. Through this process, the styrene acts as the bridge between polyester chains to form the cross-linked network (2).

Unsaturated polyester resins will gel on their own with time, however not within a practical timeframe for manufacturing, resulting in the need for the catalytic activation. In the polyester cure reaction, the speed of cure is controlled by the quantity of reactant as well as the cure temperature.

### 2.2.4 Defining the Stages of Cure

The cure of thermosets refers to the chemical process that is the cross-linking of polymer chains to form a rigid and infinite 3D network of increased molecular weight as the liquid resin is transformed into the solid thermoset, as described for epoxy
and polyester in the previous section. During cure there is a change in chemical structure and properties that results in a secondary change in physical properties, which is irreversible in thermosetting polymers.

The stages of cure are shown in the flow chart in Figure 2.7. From the liquid resin stage, the start of the cure process is initiated either by heat, irradiation or a chemical reaction. As the exothermic reaction proceeds, polymer cross-links form continuously and eventually create an infinite network. This is described as the gelation point. At this point, the material changes from the viscous liquid to the elastic gel or rubber state and the polymer will cease to flow. As cure proceeds, the number of 3D crosslinks and the molecular weight of the polymer will continue to increase until the thermoset reaches the solid state, which is described as

![Flow diagram of the stages of thermoset cure](image-url)
vitrification. Vitrification has been defined as the point at which the glass transition temperature and cure temperature are equal. (3) The polymer then proceeds to the end of cure, at which point no new crosslinks can be formed at that temperature. Further heating can either result in further cure of the material or degradation, in which the polymer chains become damaged by scission. In general, a higher cure temperature will result in an increase in rate of reaction for cure (2).

Industry typically uses a two-step cure cycle for thermoset-based composites. In the first stage, the composite is heated to reduce the viscosity of the resin and allow resin to flow and allow release of volatiles and gases. In the second stage, the temperature is raised to the cure temperature and held until completion of the cure reaction. It is necessary to have a good understanding of the material state of cure during this process to ensure efficiency and effectiveness of the two stages, as well as the high quality of the final product.

For the manufacture of composite materials, the polymer matrix can be incorporated into the reinforcement in a number of processes prior to the cure stage. These processes include wet lay-up, spray-up, compression moulding, injection moulding, resin transfer moulding (RTM), vacuum infusion, filament winding, pultrusion and pre-impregnation (prepreg). In wet lay-up, layers of resin and reinforcement are built up in the component mould. Spray-up works in a similar way in that the fibre and resin are sprayed directly into the mould. In compression and injection moulding, the fibres and resin are placed in a preheated mould and the composite is cured under pressure. RTM also uses a hot mould, where in this instance the fabric is placed in the mould and the resin is injected under pressure. In filament winding and pultrusion, fibres are fed through a resin bath. Prepreg consists of a fabric which has been previously impregnated with catalysed resin and partially cured. Prepreg PMCs must be stored at low temperatures of around -20°C to prevent further cure during storage. During the manufacture of PMCs, with the exception of prepreg, there are two key stages for which understanding of cure state is vital – resin infusion and composite cure. For material which has not been previously impregnated, the resin must first be infused through the fibres in tows, mats or fabrics. Throughout resin infusion, the matrix resin must be of low enough viscosity to ensure even distribution through the reinforcing material. In order to achieve this, it is necessary for infusion to be complete prior to gelation and full cure (4). A number
of different methods have been proposed to define the gel point experimentally, however there remains scope for improvement in the way the gel point is defined and measured (2, 5).

2.3 Online cure monitoring

The previous section introduced the cure mechanisms and stages of cure during processing for epoxy and polyester resins, two popular thermoset resin systems used in the manufacture of polymer matrix composites. In this section, a review of the state of the art in cure monitoring techniques is presented, undertaken in order to establish a complete view of the methods used to measure the degree of cure of composite materials.

Achieving full cure in the manufacture of composite materials remains a challenging task due to the nature of composite manufacture, as the final cured parts are often composed of large and complex geometries, creating the potential for uneven impregnation and cure throughout the material. Exotherms caused by the cure reaction can further complicate the cure process by significantly raising the internal temperature of the composite. As a result of these issues, industrial manufacturing methods are often conservative with cure temperatures and times, using high safety margins during processing. This is both costly and could cause a reduction in material ductility though overcuring and therefore degradation.(5)

Characterisation of the cure state of thermosets is of fundamental importance to the manufacturing process of polymer matrix composites, ensuring quality and performance of the finished product. Methods for the characterisation of cure can be separated into two categories; online cure monitoring and offline cure measurement. Online cure monitoring can ensure that the cure process is both effective and efficient by providing the opportunity for a live feedback loop, which offers the potential for increased product quality through delivering a more even and complete cure, as well as the ability to compensate for changes that may have occurred in the resin during storage. In addition, the cure process can be optimised through time and energy savings. This type of online cure monitoring would require a non-destructive analysis technique. In contrast, offline cure characterisation takes
place in the laboratory and can provide information on the required cure cycle or assessment of the final product. Offline cure characterisation can be either a destructive or non-destructive technique.

Cure monitoring technologies have been researched widely since the 1980s and a number of potential techniques have been identified which measure different material properties that vary as a function of cure state. Through these techniques, the thermoset cure process has been characterised as a measure of heat flux, direct chemical changes or indirect physical changes. The type of measurement can, in general, further be categorised as either dielectric, optic fibre, ultrasonic, infra-red, thermal, or mechanical, however at present only thermal, dielectric and optic fibre methods are used in industry processes. There is currently poor agreement between these different cure measurement techniques, as reported in a Measurement Note published by NPL (6).

Dielectric analysis (DEA) is one of the most widely researched methods for online cure monitoring (7-11). The DEA measures changes in permittivity as a result of decreasing mobility of ions and dipoles during cure. Figure 2.8 shows the relationship between the dielectric loss factor and the degree of cure, as reported by Boll et al. (12). DEA can be used to monitor the entire cure process and is popular owing to its sensitivity to changes in degree of cure, which is higher than optical methods (13). This technique does not require specific specimen geometry, making it particularly suitable for use during industrial processing. Bang et al. (14) used dielectrometry to measure the degree of cure of GFRP, which was found to have an error of less than 3% when compared with the results of differential scanning calorimetry (DSC) measurements, where DSC is the most recognised method of measuring the degree of cure. Dimopoulos and co-workers (15) demonstrated a good correlation between the impedance maxima obtained from dielectric cure measurements and the degree of conversion obtained using DSC. For DEA measurements, dielectric sensors can either be embedded within the composite or mounted within the mould, press or as part of another piece of characterisation equipment. Skordos and Partridge (16) identify one of the key issues relating to the uptake of dielectrometry for the use of industrial cure monitoring as the complexity of analysis, where more established methods such as DSC are simpler. DEA has
been compared with DMA and DSC by Stark (17), however no values are given in this work to identify the degree of agreement between the techniques.

Figure 2.8: Relationship between loss factor and degree of cure (12)

In addition to DEA cure monitoring, Fibre-Bragg Grating (FBG) sensors have been studied extensively as a tool for measurement of cure state (18-20). These optic fibres are embedded within composite laminates and the wavelength shift is measured as a response to the changing strain on the sensor during cure. The strain can be linked to volumetric shrinkage caused by changes in chemical bonding of the polymer, which has been attributed to the gelation and vitrification points. FBG sensors have been researched not only for their potential cure monitoring capability, but also for strains resulting from the cure process, which was compared by O’Dwyer et al. (21) with DEA to link the strains to the stages of cure, who found that combining these techniques made it possible to monitor the development of internal strain and identify a cure profile to minimise this effect. In addition to examining the strain changes during manufacturing, FBG sensors have been used for structural health monitoring of composites, and therefore have potential as a useful means of monitoring composite components throughout their life (13, 22). One of the key limitations of this technology, however, is that FBG sensors are a complex and expensive method to implement.

Another technique currently being studied is the use of ultrasonics, which offer the potential as either an online or offline cure monitoring technique. There are two types of ultrasonic method used for cure monitoring purposes. The first is ultrasonic
time-of-flight, which measures the time delay of a wave that is directed through the sample by either being pulsed and echoed back or simply transmitted through. The time of flight of the wave is proportional to the longitudinal modulus of the sample, which increases during the cure process, while the attenuation of the wave is proportional to the viscosity of the sample. Measurement of these properties can be used to provide information on the state of cure (6). The second type of ultrasonic measurement measures the velocity of a laser-induced acoustic wave. One of the limitations of ultrasonic cure monitoring is that it requires a closed mould, although Lionetto et al. (23) report the potential for a non-contact method. Liebers et al. (5) showed that the ultrasound method could be combined with rheology in order to calibrate the ultrasound technique in the laboratory for application as an offline technique.

Fourier transform infrared spectroscopy (FTIR) has been popular in recent literature as a method of cure monitoring. In an FTIR spectrometer, light is directed at a sample, and some of this radiation is absorbed while some is transmitted. A spectrum of the absorbed and transmitted light is then produced, where different chemical groups absorb energy from different wavelengths. This allows the user to track the chemical changes within the sample based on changes in the signal.

FTIR is currently used offline in the laboratory by chemists to characterize the cure cycle in the design of industrial cure processes (24). FTIR provides a direct measure of the chemical changes that occur during the cure of PMCs. This method could prove to be a useful tool for online cure monitoring as it can be used to monitor and assess the chemical reactions which occur during cure, thus providing a deeper understanding of cure mechanisms at different points of conversion. One of its limitations, however, is that FTIR does not provide information on the material properties, such as $T_g$ (25).

Zhang et al. (26) successfully used FTIR to monitor the degree of conversion during cure of a glass-epoxy prepreg material typically used in printed circuit board manufacture. The results were comparable with DSC measurements, which is the common practice method for calculating the degree of conversion. Figure 2.9 demonstrates the evolution of the NIR spectra during cure, showing clearly the decreasing peak at 4530 cm$^{-1}$. The near-infrared spectrum band 4530 cm$^{-1}$,
attributed to epoxy group vibrations, is typically used to monitor the progression of cure. In this study, Zhang et al. found that the phenyl peak at 4613 cm\(^{-1}\) remained constant, and so used this as a reference to obtain the degree of conversion from the epoxy peak, stating the degree of conversion, \(\alpha\), as

\[
\alpha = \frac{\text{Area under epoxy peak at given time}}{\text{Area under phenyl peak at given time}} \times \frac{\text{Area under epoxy peak at origin}}{\text{Area under phenyl peak at origin}}
\]

Braun et al. (25) compared FTIR with DSC and TGA data in order to identify the cure, decomposition and glass transition temperatures. Attenuated total reflection (ATR) FTIR was used to identify the model chemical changes during the cure of an epoxy resin, shown in the spectrum in Figure 2.10. The nitrile and oxiran chemical groups which have been identified in the spectrum of the uncured resin (below) can no longer be seen in the spectrum of the cured resin (above), signalling that the cure reaction described in 2.2.2 has occurred. The effect of temperature on signal intensity for several chemical groups was studied in order to characterise chemical changes of the cure process. These results were not linked to material properties such as \(T_g\) or degree of cure.

![Figure 2.9 - Absorbance obtained from FTIR of PCB material (26)](image-url)
Lin *et al.* (27) compared DSC with IR data and identified a link between observed chemical changes and exotherms. Lachenal *et al.* (28) were able to use a combined FTIR and DEA to identify the vitrification point. Mijovic *et al.* (29) compared FTIR and DEA as measures of cure conversion in an epoxy/amine system and found good correlation between the two techniques. These studies show promise as a new way of monitoring cure by combining FTIR with indirect analysis techniques.

Other studies include Raman, nuclear magnetic resonance (NMR) and fluorescence as potential methods for monitoring cure (30-33)(11). Rheometry has been commonly used to monitor cure in past studies, (34-36) but is only suitable for analysis prior to the vitrification point, and therefore unsuitable for the monitoring of the whole cure process.

Recent research is focused on the development of these measurement techniques for feedback-loop control to be used online during processing. Current cure control technology relies on thermocouples which monitor different areas within a system (oven, autoclave, etc.) and provide feedback to the program, however these can only provide a measure of temperature rather than the direct changes in cure state (chemical information) or resulting changes in physical properties (5).
2.4 The $T_g$ as an indicator of cure

The previous section presented some of the measurement methods being developed for use in online cure monitoring. Advancement and uptake of these relatively new techniques relies on comparison with established cure measurement methods such as dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC), which are three types of thermal analysis technique. Thermal analysis is the measurement of changes in material properties when subjected to a controlled heat profile. One of the material properties most regularly measured by thermal analysis is the glass transition temperature, or $T_g$. The glass transition region occurs over a temperature range and marks the region in which the behaviour of a material changes from glassy to rubbery with increasing temperature. In the glassy state, local molecular mobility is restricted, where chain rotation cannot occur due to insufficient thermal energy and as a result its structure is frozen into position. As a material is heated, translational and rotational motion become possible. The $T_g$ is a point within this transition region, frequently referred to in the literature as the alpha transition (37, 38), that is used as a means of usefully representing this change with temperature. The $T_g$ is often defined as the onset of long-range segmental motion (39).

As the temperature is increased through the $T_g$, chemically crosslinked, thermosetting polymers will reach a rubbery plateau whilst thermoplastics will begin to flow. Further heating past the $T_g$ of a thermoset polymer results in irreversible damage to the chemical crosslinks and therefore degradation, unlike thermoplastics which eventually achieve melt when heated above the $T_g$. The $T_g$ is therefore an important thermal property of composite materials which is frequently used to help define a suitable service temperature, given by an offset from the measured $T_g$, (in addition to considerations for the environmental performance of the material).

During cure, thermosetting polymers undergo many physical property changes associated with the chemical changes (i.e. increased crosslinking) that result from the cure process, including an increase in $T_g$. Consequently, the $T_g$ can be used as a convenient indicator of the cure state of a composite material.
In the initial liquid resin stage of the cure process, the $T_g$ is lower than the cure temperature, $T_{\text{cure}}$. As cure proceeds up to the gelation point, the elastic modulus remains low, while the viscosity of the resin undergoes a drastic increase. Once the resin reaches the gel point, the glass transition temperature rises sharply, as described by Paroli and Penn (40). When it has reached this point, the material is able to sustain in-plane shear stresses (41). With increasing degree of cure, also known as conversion, the glass transition temperature continues to rise until the vitrification point, when $T_g = T_{\text{cure}}$ and the material moves from the rubbery to the glassy state. As this happens, the elastic modulus undergoes a large increase (41). In a Measurement Note published by NPL, full cure is defined as the stage at which the $T_g$ has reached a constant value (6).

As the glass transition temperature continues to increase throughout the cure process, it can be used as a reliable indicator of the degree of cure of a polymer matrix composite (42). The glass transition temperature is typically measured using DSC, DMA or TMA. Bussu (43) describes the glass transition temperature as an “appealing metric” as it gives information on the chemical and physical state of the material, mechanical properties and performance, useful for both development and quality control.

Several authors have studied, experimentally, the relationship between degree of cure and the glass transition temperature. Carbas et al. (44) found an increase in $T_g$ with degree of cure up to a plateau, which they measured by DMA, however they have not attempted to quantify this relationship. Vo et al. (45) found a positive relationship between the $T_g$ (measured by DMA) and the degree of cure (measured by DSC). In this work, the authors have used the $T_g$ as an indicator of the degree of cure for comparison with the strength measured by short beam shear. Their findings, reproduced in Figure 2.11 for reference, show that strength increases linearly with $T_g$ and hence degree of cure. It is therefore of importance that engineering polymers and polymer matrix composites are cured fully prior to service, in order that they achieve their full design properties. In particular, the aerospace industry requires a near-100% degree of cure for composite parts. (46) It would be valuable to further develop understanding of the relationship between the degree of cure and shear strength, as this work has shown the potential of
mechanical testing as a means of quantifying degree of cure. This would be particularly useful for quality control purposes.

Figure 2.11: Relationship between degree of cure and $T_g$ (shown on the left) and between strength and $T_g$ (shown on the right) (45)

Stark et al. (46) investigated the potential of DMA as a method for quantifying the degree of cure of epoxy-based CFRP prepregs. The authors describe a major disadvantage of cure characterisation by DSC as the occurrence of an overlap between transitions; specifically, the glass transition and the exotherm associated with crosslinking (cure). Further, that the heat of reaction at higher degrees of cure is too low for precise measurement. Alternatively, they have shown in their work that DMA is a more precise way of measuring high degrees of cure using the loss modulus peak as a measure of $T_g$.

In their review of the literature, Hagen et al. (39) found that the $T_g$ measured by DMA at a frequency of 0.01 Hz is equivalent to that measured by DSC at a heating rate of 10 K/min. In light of this the authors have extrapolated their frequency data to obtain a $T_g$ at this frequency using the linear relationship that was found between frequency and $T_g$. They related this to the degree of cure as measured by DSC as a useful means of calculating the degree of cure from $T_g$ data obtained by DMA.

Billotte et al. (47) used a novel adaptation of the DMA technique in order to measure heat flux changes alongside the mechanical and dimensional changes which occur during cure, with the purpose of relating the $T_g$ measurement by DMA to the degree of cure. In this method, a DMA was adapted using a “heat flux cell” which consisted
of metal plates that hold the DMA specimen while acting as heat flux sensors. The shrinkage was measured by monitoring the position of the upper enclosing plate. This would not be a practical technique for on-line use and does not probe the direct chemical changes, but can provide useful information in laboratory studies.

Pang and Gillham (48) studied the competing mechanisms of cure and degradation in an epoxy resin system when cured at high temperatures, indicated by the variation in T_g measurement using torsional braid analysis, heating the resin up to 240°C for an epoxy of cure temperature 100°C, with a maximum T_g of 171°C. In their work they showed that the T_g can be used as a reliable indicator of the advancement of cure. Whilst T_g and degree of cure increase with cure temperature, it was concluded that it is not possible to achieve complete cure, and at high temperatures there is competition with degradation.

In addition to experimental studies, many have attempted to model the relationship between degree of cure and the glass transition temperature using the DiBenedetto equation;

\[
\frac{T_g - T_{gu}}{T_{gu}} = \frac{\left(\frac{\epsilon_\infty}{\epsilon_0} - \frac{c_\infty}{c_0}\right)x}{1 - \left(1 - \frac{c_\infty}{c_0}\right)x}
\]

Where T_gu is the glass transition temperature of the uncrosslinked polymer, \(\epsilon\) is the lattice energy, \(c\) is the segmental mobility, \(x\) is the crosslink density and the notations 0 and \(\infty\) indicate either no crosslinking or full crosslinking, respectively.

This equation was originally published by Nielsen in 1969 (49), however in a further paper (50), DiBenedetto himself has questioned whether this approach is suitable for highly crosslinked materials. In their 1990 paper, Pascault and Williams (51) reconsidered the DiBenedetto equation as a means to relate T_g to degree of cure. The authors state that they have considered that experimental measurements of T_g can be affected by the heating rate used. The T_g values in this study were obtained from existing literature, and whilst the lack of precision in T_g measurement is raised as an issue, no compensation for this variation has been made in the calculations.

Hale et al. (52) compared experimental data for the degree of cure and T_g of a crosslinked novolac-epoxy resin system, which could not be fitted to the
DiBenedetto equation. The authors produced an alternative model, which assumes that the increase in $T_g$ with cure is caused by a reduction in chain-ends, formation of crosslinks and a decrease in configurational entropy. Their model and experimental data showed good correlation and an increase in $T_g$ with degree of cure. Conversely, Khoun et al. (53) measured the relationship between $T_g$ and degree of cure using modulated DSC and found that their results were a good fit to the DiBenedetto equation.

Min et al. (54) used two separate terms for the glass transition temperature in their model, with the first being a function of the extent of the linear polymerisation reaction and the second as a function of the crosslinking reaction. The authors used both near-infrared spectroscopy and DSC to measure the degree of cure as a function of time for an epoxy system. DSC was used to measure the glass transition temperature. They found good correlation between their model and the data, which the authors show to be a suitable alternative to the DiBenedetto equation when applied to crosslinked thermoset systems.

2.5 Measurement of the glass transition temperature

2.5.1 Introduction

In the previous section it was shown that the $T_g$ is a well-known indicator of the degree of cure of a polymer. There are a variety of techniques available for measurement of the $T_g$. The three major techniques for measurement of the glass transition temperature are dynamic mechanical analysis (DMA), thermomechanical analysis (TMA) and differential scanning calorimetry (DSC), which were briefly introduced in the previous section. It is well-known that different values of $T_g$ are obtained for the same material when using different measurement techniques (55-59). Within each of the techniques, there are, in addition, numerous ways of obtaining and identifying the $T_g$ within the glass transition region from variations in experimental setup to different data analyses. The theory, advantages and drawbacks of DMA, TMA and DSC are discussed in this section.
2.5.2 Dynamic mechanical analysis

DMA is a popular technique due to its relative speed (38, 43, 60) and high sensitivity to the glass transition (42). This technique takes advantage of the change in modulus and damping properties of a material at the glass transition temperature, where the onset of chain movement results in an increase in free volume, allowing molecular motion to occur more freely (61). In this test method, the specimen is placed inside the DMA furnace and subjected to a controlled heating profile. The sample can be clamped inside the furnace in a number of deformation modes, including single-cantilever, dual-cantilever, tension and three-point bend. Throughout the test, the specimen is subjected to sinusoidal mechanical deformation that induces a stress, $\sigma$, which results in a corresponding strain, $\varepsilon$, which is out of phase with the sinusoidal stress by angle, $\delta$. The phase lag between stress and strain occurs as a result of the viscoelastic response of the material. (42)

The complex modulus can then be calculated using

$$E^* = \frac{\sigma_{\text{amplitude}}}{\varepsilon_{\text{amplitude}}}$$

Using this information, the storage modulus, $E'$, loss modulus, $E''$, and $\tan \delta$ values can be derived following the relationships:

$$E' = E^* \cos \delta$$

$$E'' = E^* \sin \delta$$

$$\tan \delta = \frac{E''}{E'}$$

During analysis, the storage modulus, loss modulus and $\tan$ delta are presented on separate axes as a function of temperature. The glass transition is directly related to the crosslink density and storage modulus, and can be seen as a step change in the storage modulus of the material on this graph. This is shown in Figure 2.12, where the $T_g$ is taken as the inflection point of this curve. The values of loss
modulus, which represents the energy dissipated as heat, and tan delta, which represents damping, are also presented against temperature on the graph in Figure 2.12, where the glass transition temperature may also be interpreted as either the peak of the loss modulus curve or the peak of the tan delta curve. In addition to these three analysis points, the onset point of the storage modulus curve is occasionally used as a value for T_g.

The choice of analysis point used to record the glass transition temperature varies between users, however these measurable points (i.e. peak loss, peak tan delta, storage modulus inflection point), occur at different temperatures which can affect the precision of how T_g data is reported (59). Typically, the storage modulus inflection point will give the lowest value, followed by the loss modulus peak. (39, 42) The tan delta peak will generally provide the highest value in PMCs and is the most sensitive to incomplete cure, which would be observed as a second peak or split peak. Hagen et al. (39) highlight that the tan delta is related to the damping and is not associated with the onset of segmental motion.

In addition to the variety of analysis points available, there are many parameters that can be customised during setup of the DMA. These include frequency, displacement, load and heating rate (42, 62). The degree of flexibility in how a DMA test method can be set up and executed results in a number of ways in which the measured T_g value can be affected. It is noted by Paroli and Penn (40) that “care should be taken when reporting the glass transition temperature obtained by DMA” due to the influence of frequency, heating rate and analysis point used, whilst Li et al. (42) showed that higher test frequencies result in a higher value of T_g among other issues which can affect T_g measurement (such as heating rate) and describe the measurement of degree of cure as “subjective” due to these effects. Placet et al. (63) state that the T_g can vary due to thermal lag as well as choice of analysis point. Further to the details of the test setup, Hagen et al (39) raise the issue that discrepancies in T_g can be found between different instruments or laboratories as a result of variations in specimen dimensions, mechanical inertia, clamping effects, heating rate and chamber environment. Bussu and Lazzeri (43) found that results were not repeatable on two different instruments, suggesting that current test standards do not adequately mitigate for these differences.
Of the DMA test parameters that can be controlled, the impact of changing the test frequency in DMA measurement of $T_g$ has been one of the most widely studied. This is described well by Ornaghi et al. (64), who describe the viscoelastic properties of a material as dependent upon both temperature and time, and thus frequency, suggesting that in DMA tests one of these elements should therefore be kept constant. The authors found an increase in the $T_g$ with frequency of approximately 15°C for a frequency range of 1 Hz to 30 Hz in DMA tests of polyester/sisal/glass composites. The authors have correlated these data with the well-known Arrhenius relationship, which is often used to calculate the activation energy, $E_a$, of the glass transition. In addition to Ornaghi et al, a number of authors describe the use of a multiple frequency approach to calculate the activation energy, where the frequency is then plotted against temperature and the slope of the fit line used to find $E_a$ (37, 40, 42). Paroli and Penn (40) suggest a DMA multiplexing experiment could be used to prove that the mechanical response observed by DMA is a real $T_g$ from the activation energy.

Hagen et al (39) studied the frequency dependence of $T_g$ using two makes of DMA instrument and showed that the frequency dependence of $T_g$ was similar for the two...
Instruments compared. Placet and Foltête (63) studied DMA as a resonance technique and produced a model to mitigate the effects of resonance and assist in selection of a test frequency. However, as shown here, the influence of changing the test frequency on DMA measurements of $T_g$ has been widely studied and it is well known to affect DMA test data. As a result, it is common practice to use a test frequency of 1 Hz, which has become widely recognised as the standard setting, and is referenced in ISO 6721-11 (65).

In addition to the test frequency, it has been extensively reported that thermal lag can influence $T_g$ measurement by DMA. Several authors have studied the relationship between heating rate and thermal lag and found that a faster heating rate leads to an increase in thermal lag and therefore a higher reported $T_g$ (37, 38, 42, 62, 66, 67). Thermal lag is caused by the discrepancy between the temperature measured by the instrument thermocouple and the true temperature inside the specimen (62). The degree of thermal lag can be influenced by a number of factors, including specimen dimensions, thermal conductivity of the specimen, and the instrument clamps (42).

Pinheiro et al. (38) studied the effects of thermal lag on DMA measurement of the $T_g$ of poly-DL-lactide (PDLLA) and found a difference of approximately 8°C using heating rates ranging from 0.1 to 4 K/min. In this work, the authors used a reference specimen containing an indium core to apply a correction factor to the test results. Indium has a well-characterised melt temperature of 156.6°C and this melt point can be seen clearly in a DMA graph, therefore the difference in the observed melt temperature and the known melt temperature can be used as a correction factor, however the authors note that this may not be possible at higher heating rates due to discrepancies between the thermal conductivities of the indium and the PDLLA.

In order to minimise the effects of thermal lag, Li et al. (42) propose a maximum test heating rate of 2 K/min, and have showed that the Arrhenius law for calculation of the activation energy of the $T_g$ is only applicable to heating rates lower than this. One of the major drawbacks of this proposal is the increased test time, which may not be practical in an industry setting, and at best adds extra costs, particularly for quality control testing.
Sućeska et al. (62) used heating rates ranging from 1-10 K/min to study the relationship between T_g and heating rate. The authors show that the increase in T_g with heating rate follows a linear relationship and have used this to extrapolate for the T_g at zero heating rate, which they describe as the true glass transition temperature, i.e. independent of thermal lag effects. Here, the authors have quantified the thermal lag as the T_{furnace} – T_{sample}, and shown that this lag increases with heating rate. The authors modelled heat transfer in the DMA and found good agreement with their experimental results, but have not proposed a simple method for the practical application of their findings. The authors noted the complexity in deriving experimentally the values for the heat transfer coefficient they have used in modelling, as this depends on multiple parameters, including specimen geometry and the heat transfer mechanism present in the system. Some of these parameters can change with temperature, such as the thermal conductance of the fluid within the furnace.

Lacík et al. (67) discuss thermal lag in the DMA with a focus on rubbers (for tyres). The authors explored a number of possible heat profiles during testing with the aim of obtaining more precise mechanical property data. These include use of isothermal and slow heating rate tests, as well as maintaining an isotherm around the T_g. They tested in bending as well as vertical and horizontal tension, and found that the effect of heating rate was lesser in horizontal tests, attributing this to boundary layers and temperature gradients within the furnace. It is proposed that the temperature profile of a sample at any time can be calculated with a Fourier equation based on sample thickness and diffusivity. The authors found that sample length has more effect than thickness when testing in tension. The authors have highlighted that it is important to characterise the effects of thermal lag for correct data interpretation.

Cristea et al. (37) studied the effects of varying the heating rate in DMA tests on the alpha transition while maintaining a constant frequency of 1 Hz. They found an 8°C variation in T_g for heating rates ranging from 0.5 to 4 K/min. The authors found that the effect of thermal lag can be mitigated by matching the heating rate to a corresponding frequency using a formula by Jäckle (68).
Whilst numerous studies have been performed on the effect of heating rate on thermal lag and therefore measurement of \( T_g \), a universally applicable heating rate has not been agreed upon. This has been addressed in the recent standard, ISO 6721 – Part 11: Glass transition temperature (65), which was published as a result of recent research conducted at NPL. In this standard, a novel technique is presented for the determination of the \( T_g \) of plastics using DMA. When measuring \( T_g \) in the DMA, it has been proven that a heating-rate dependent lag has resulted in all previous methods overestimating the value of \( T_g \). This new method aims to discount the effects of thermal lag during testing and was designed as a complimentary technique to DSC measurement of the \( T_g \). In this new method, specimens are heated in the DMA up to a minimum of 50°C above their \( T_g \) using an oscillation frequency of 1 Hz. Tests are performed at linear heating rates of 3, 5 and 10 K/min. The values for the \( T_g \) are taken as the inflection point of the decrease in storage modulus from the graph of storage modulus against temperature. These are subsequently plotted on a graph of heating rate against \( T_g \) and the data is then extrapolated using a linear fit in order to determine the predicted \( T_g(0) \) at a heating rate of 0 K/min, as shown in Figure 2.13. This line is defined in the standard as the calibration curve, which can be used to determine the \( T_g \) for data collected at any heating rate using the same material and instrument. Using the calibration curve, materials can be tested at faster heating rates to reduce test durations whilst accounting for thermal lag. For each individual material and instrument a new calibration curve must be produced. Use of the value \( T_g(0) \) aims to increase consistency and precision in the measurement and reporting of the value of \( T_g \). The experimental work that contributed to this standard showed that the inflection point of the storage modulus curve produced the most repeatable data, however, in line with industry practices, the standard dictates that the test report must include the graphs of the storage modulus, loss modulus and tan delta with the analysis points indicated in Figure 2.13 as well as the extrapolated value for \( T_g(0) \) and the accompanying calibration curve.

The new method was verified in an interlaboratory trial using a specially designed indium specimen produced at the National Physical Laboratory. This specimen consists of a CFRP composite with an indium film embedded at its centre, which is similar to the work of Pinheiro et al. (38) discussed earlier in this chapter. Using this
specimen, a clear change in the DMA loss modulus signal is observed at the melting point of the indium, seen in Figure 2.14, providing an indication of the true temperature at the centre of the specimen as opposed to the temperature measured within the furnace. In the interlaboratory trial, these indium specimens were subjected to testing at six independent sites following the methods outlined in ISO 6721-11 at heating rates of 1, 3, 5 and 10 K/min. The results are shown in Figure 2.15, where the maximum deviation from the true melting point of indium was 1.2°C. The near-convergence of the calibration curves at 0 K/min at a temperature value within 2°C of the melting point of indium was used to demonstrate the validity of this technique.

![Figure 2.13: Determination of T_g(0) at 0 K/min from calibration curve (65)](image)

![Figure 2.14: Graph demonstrating sharp drop in loss modulus during indium melt (65)](image)
In addition to the choice of heating rate, another parameter that could influence the degree of thermal lag in DMA measurements is the specimen dimensions. This was addressed in a recent paper by McAninch et al. (69), who highlighted that the only test standard in which specimen dimensions are described in detail is ASTM D5023. The authors found that there was a positive correlation between specimen thickness and $T_g$ value. The authors suggest that this could be due to reduced thermal lag in the thinner specimens, however they conclude that the sample sizes used were not large enough for the results to be significant. It was found that samples tested in tension had an even lower $T_g$, attributable to a lower thermal lag as a result of the thinner specimens used in this type of test and/or a difference in thermocouple placement with respect to testing in the cantilever formation. In addition to specimen thickness, the authors studied the effects of changing the clamps between dual cantilever, single cantilever and three point bend and found that this did not cause variation in the $T_g$. In the conclusions, they state that the $T_g$ is sensitive to sample dimensions due to thermal lag, so whilst the clamp arrangement themselves do not alter the $T_g$ value, the difference in specimen dimensions and thermocouple position must be considered. In their review of the literature they found that information on the specimen thickness was often left out, among other test parameters, concluding...
that many researchers are “unaware of manufacturer recommendations”. This could be mitigated by a clearer picture of what is key to obtaining good data and better test standards. Whilst the authors focused on modulus measurements, the work in this thesis will focus on measurement of the Tg. A systematic study on the effect of thickness on Tg measurement has not been reported in the literature, as such it would be worthwhile to expand on this work and form a clearer picture of the relationship between specimen thickness, thermal lag and Tg.

In addition to specimen thickness, fibre orientation and sizing have been explored in the literature as factors which may impact the measurement of Tg. Bussu and Lazzeri (43) examined the significance of fibre orientation and load on the measured values of Tg. Tests were performed using two unidirectional CFRP materials cut in the transverse and longitudinal direction. In a three point bend test it was found that a higher preload reduced the measured Tg value when specimens were tested with the fibres transverse to the length. It was suggested that this is due to an increase in free volume and molecular mobility at higher preloads, noticeable only in the orthogonal direction where the test is matrix-dominant. They reported that any differences between longitudinal and transverse testing were due to the difference in preload value. This issue is not addressed in current DMA standards.

Costa et al. (60) report changes in Tg due to varying the sizing of fibres and thus altering the interfacial adhesion of fibre and matrix, which is visible through variations in tan delta peak height. They also report that the Tg increases with the volume fraction of fibres due to reduced chain mobility.

Ormaghi et al. (64) found that increasing fibre content gave a higher activation energy and therefore higher Tg due to “segmental immobilization of the matrix chain at the fibre surface”. These effects can both be attributed to changes in the inherent Tg of the material and are different from an increase in Tg which occurs as an artefact of the test. When assessing factors that can affect the measurement of Tg it is important to note this distinction.
2.5.3 Thermomechanical analysis

Thermomechanical analysis (TMA) is another long-standing method for measurement of the $T_g$ (70). In thermomechanical analysis, the dimension change of a material is measured under a controlled heating programme. As with the DMA, there are a number of modes in which the TMA can be used, namely expansion, compression, flexure and extension. In compression mode, which is the setup used in this work, a static load is applied through a probe to the sample while undergoing a controlled temperature programme, as shown in Figure 2.16. The load exists to maintain contact between the probe and the sample. As the temperature rises, the sample expands and this change in dimension is fed back through the probe and measured. A change in the gradient of the dimension change with temperature, also known as the coefficient of thermal expansion (CTE), can be observed at the $T_g$, which is taken as the midpoint of this change. A change in CTE is observed at the glass transition due to the onset of polymer chain movement, which causes a rise in the free volume of the material and therefore an increase in specimen dimensions. A typical TMA plot and analysis for a PMC is given in Figure 2.17, showing the $T_g$ at the midpoint point of the curve.

![Schematic diagram of TMA in compression mode](image)

Earnest (70) described this method as unrepresentative of the true sample temperature, due to the nature of the temperature measurement, where the instrument thermocouple is placed near to the specimen. The author describes a number of calibration procedures using the known melting points of different materials, however this cannot account for differences in thermal conductivity between materials, therefore calibration using one type of material does not
necessarily relate to another and cannot compensate for thermal lag effects in specific test specimens. The method using multiple heating rates outlined in DMA test standard ISO 6721-11 could be applied to mitigate the effects of thermal lag. The author suggests that thermal lag is also increased with specimen thickness.

Cadenato et al. (71) used TMA, rheology and DSC to examine the gelation time of an epoxy resin. The method used was to apply a periodic force with the TMA until the amplitude dropped significantly, which was taken as the stage at which the probe had “set” inside the resin, thus indicating the resin had gelled. This was then compared to the results from the rheometer. In both instances, the epoxy was rapidly cooled at the interpreted gel point and the degree of conversion measured using DSC. These results gave different gelation times for the epoxy resin and difference in degree of cure.

Paroli and Penn (40) describe two of the drawbacks of TMA testing as the need for proper calibration and the occurrence of probe slippage during testing, however they have not studied this in their work comparing TMA with DMA and DSC.
Foreman et al. (72) suggest that there are multiple options for calibration of the TMA, including calibration to the material being tested, as well as calibration of the instrument as was suggested by Earnest (70). As such it is difficult to compare data obtained by different TMA instruments, resulting in poor data reproducibility.

2.5.4 Differential scanning calorimetry

![Schematic diagram of DSC](image)

Figure 2.18: Schematic diagram of DSC

The differential scanning calorimeter is a thermal analysis technique which measures the difference between the energy required to raise the temperature of a sample and a reference when subjected to a controlled heating profile. This method is used to measure enthalpy changes during heating of the sample in order to identify the temperature at which significant events occur, such as crystallisation and $T_g$. A schematic diagram is presented in Figure 2.18 showing the setup of the instrument within the furnace for a power compensated DSC, such as the one used later in this thesis. The thermocouples measure the sample and reference heat flux. The $T_g$ can be observed as the energy absorbed to change state, as depicted in the schematic diagram in Figure 2.19. The diagram shows an example graph of the data output of the DSC, where the heat flow is plotted against temperature. The glass transition temperature is typically taken to be the inflection point of the endothermic step change as shown.
In addition to measuring the $T_g$, the DSC is the traditional technique used to measure degree of cure (otherwise known as conversion).(42) The cure reaction produces an exotherm which can be measured by the DSC, and the degree of cure calculated using the following equation:

$$\text{Degree of cure} (\%) = \left(1 - \frac{H_S}{H_T}\right) \times 100$$  \hspace{1cm} (2.1)

where $H_S$ is the heat of reaction of the partially cured specimen and $H_T$ is the total heat of reaction. Error! Reference source not found. demonstrates a schematic diagram of a DSC curve for the curing of an epoxy thermoset. The largest peak, highlighted in green, is known as the crystallisation peak, where $H_S$ can be calculated from the area under the curve. $H_T$ is calculated in the same way, from DSC analysis of the uncured resin. DSC is a well-reported and long-established method for observing the cure of polymers in the laboratory. While it is unsuitable for in-situ and on-line use in industry, DSC is often used to obtain a baseline for comparison or as a validation for other techniques. (11, 14)
Modulated DSC is a variation on the standard DSC method in which the heating rate follows a sinusoidal wave imposed on the standard rate, as opposed to a constant heating rate. Modulated DSC can resolve some of the problems associated with the standard DSC technique, including the detection of small transitions and overlapping signals which often prove challenging for data interpretation. The MDSC separates signals from multiple transitions by providing quantitative measurement of heat capacity. Kinetic events are separated from changes in heat capacity by measurement of the total heat flow as well as the heat capacity component. This allows for improved data interpretation, where standard DSC can only provide one signal for all of the thermal events occurring at a specific temperature. Modulated DSC is the most suitable for identifying the vitrification point (73).

The effect of thermal lag in DSC measurement was studied by Hutchinson et al. (74), who describe thermal gradients in DSC testing as a cause of thermal lag. One of the sources of these gradients is stated by the authors to be instrument effects, however this work was first published in 1987 and in the period since then, instrument calibration has improved considerably. The authors showed a shift in the signal with heating rate when varied between 10 K/min and 40 K/min, however they did not quantify the effect this had on the measured $T_g$ value. Similarly, Zhang et al.
(26) used DSC to study the cure of GFRP prepregs and observed an upwards shift in exotherm peak with increasing heating rate, reporting a higher degree of conversion for higher heating rates at the same temperature.

2.5.5 Comparison of techniques

The previous three sections discussed in detail the three most common thermal analysis techniques for the measurement of $T_g$ (DMA, TMA and DSC) as standalone techniques. It has already been stated, however, that measurement of the $T_g$ using each of these techniques does not result in the same value. Many laboratories with the capability to measure the $T_g$ will only have one of these three instruments available. The effect of using different instruments on measurement precision has been discussed by different authors. Pournoor and Seferis (75) state that it is difficult to obtain precision data between different test methods, instruments and users due to the number of test parameters that could vary. Paroli and Penn (40) describe the difference between TMA/DMA and DSC as a result of the fact that they are static vs dynamic tests.

Foreman et al (72) described the cause of the difference in $T_g$ measurements between DMA and TMA as the variance in relative specimen size used for the two techniques. The authors suggested that the difference in component materials of the instruments themselves (quartz in TMA vs steel in DMA) may also have an impact on test data.

The DMA is known to be far more sensitive to the $T_g$ than DSC and TMA (59), with the DSC being the least sensitive of the three techniques (70). The difference in sensitivity between the DMA and DSC was given by Hagen et al. (39) as a factor of 1000. These authors compared the $T_g$ measured by DMA (using the tan delta peak) with DSC and found poor correlation between the values, which is described to be a result of difference in physical mechanism that is measured. This difference would have been higher than the difference between the $T_g$ taken from the storage modulus or loss modulus measured by DMA, as they are known to be consistently lower than the tan delta value. In addition to comparing DMA with DSC, the authors compared $T_g$ measurements from two makes of DMA and found differences in the
when tests were performed on the same materials following the same heat profile and frequency. It was suggested that the differences could arise from differences in heat radiation and heat transfer within the furnace. The authors have highlighted the need for standardised calibration procedures, test parameters and definition of $T_g$. Whilst this paper was published 1994 and test techniques have since improved, these issues with current DMA test methods and procedures remain relevant.

Attempts have been made by some authors to find ways to equate DMA, TMA and DSC data. Gracia-Fernández and co-workers (76) compared temperature modulated DSC (TMDSC) to DMA on the basis that, when treated to the same temperature and frequency conditions, the resulting $T_g$ measurement would be comparable. Good correlation was found between the measured $T_g$ obtained using TMDSC and DMA with this method.

In their work, Cassel and Twombly (56) attempted to find a way to measure a consistent $T_g$ regardless of whether it is measured by DSC, TMA or DMA. The authors identify one of the major issues in comparing the test methods as the elimination of the effects of thermal lag, highlighting the difference in thermal lag between the techniques. The authors used an indium reference specimen as a calibration tool to eliminate the effects of thermal lag and were able to obtain good agreement between the DMA at 0.1 Hz, DSC and TMA using this method, however the tests were only performed once, so this method cannot be described as fully validated (which the authors do address and suggest their research can be used as a starting point).

2.6 Concluding Remarks

A number of characterisation techniques are being developed for use in online cure monitoring during the manufacture of composite materials. The glass transition temperature is one property that can be used as an indicator of the degree of cure of polymer matrix composites. DMA is one of the most frequently used thermal analysis techniques for the measurement of $T_g$, however there is a current need to assess how DMA data are affected by thermal lag. Measurements of $T_g$ obtained by TMA and DSC are not in agreement with DMA data, which can create difficulties
in communication of material properties. This is especially true if the material supplier and end user are quoting the T_g from different tests. Following the outcome of the literature review, the project aims have been refined as follows:

- To carry out a systematic study in order to assess a number of parameters which can impact the degree of thermal lag, which will be quantified by the heating rate dependence using the multiple heating rate method presented in ISO 6721-11.
- To reduce test times in QA testing by enabling the use of faster test heating rates through characterisation of thermal lag.
- To assess whether DMA, TMA and DSC data are comparable when the thermal lag effects of heating rate are accounted for.
- To study the use of T_g as a measure of degree of cure using these three thermal analysis techniques.

The next chapter presents a detailed description of the experimental methods and materials used to carry out this study.
3 Experimental Methods

3.1 Introduction

This chapter covers details of the materials used, including the manufacture of those materials made in-house, followed by a detailed description of each measurement technique used in this work. These details will be key to some of the conclusions drawn at the end of the thesis.

3.2 Materials

This section outlines the details of the polymer matrix composites and polymer resins used. The materials have been grouped by matrix resin as Systems A-E to enable easier identification throughout the thesis, where they cannot be referred to by material type (e.g. CFRP), as a number of different resins and fabrics have been used.

3.2.1 System A

The System A material was a woven carbon-fibre/epoxy composite (CFRP) purchased from Goodfellow Cambridge Ltd. in plates of five different thicknesses; 0.25 mm, 0.5 mm, 1 mm, 2 mm and 3.5 mm. Details of the material composition are given in Table 3.1, however the supplier was unable to provide the $T_g$ of the materials. Table 3.1 shows that the fabric used in each different thickness of material varied, however the matrix resin was stated by the supplier to be nominally the same for each laminate, regardless of thickness. The material supplier describes some of the composite laminates as having a gloss finish on one side. This can be attributed to the effects of the metal caul plate and release film on which the material is laid when a composite panel is manufactured in an autoclave, which leaves behind a smooth finish once removed. The five different laminate thicknesses were used in order to investigate the effect of thickness on the $T_g$ and heating rate dependence. The material was tested in the as-received condition.
Table 3.1 – Details of the System A materials

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Fabric</th>
<th>$V_f, \text{ given} (%)$</th>
<th>Resin</th>
<th>Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>Undisclosed</td>
<td>50</td>
<td>SGL CE1201 or equivalent</td>
<td>Gloss on one side</td>
</tr>
<tr>
<td>0.5</td>
<td>Undisclosed</td>
<td>50</td>
<td>SGL CE1201 or equivalent</td>
<td>Gloss on one side</td>
</tr>
<tr>
<td>1</td>
<td>10 ply 0/90 core (150gsm) woven fabric on faces (200gsm)</td>
<td>55</td>
<td>SGL CE1201 or equivalent</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>0/90/90/0 core (130gsm) woven fabric on faces (200gsm)</td>
<td>55</td>
<td>SGL CE1201 or equivalent</td>
<td>None</td>
</tr>
<tr>
<td>3.5</td>
<td>5 ply core (660gsm) woven fabric on faces (200gsm)</td>
<td>50</td>
<td>SGL CE1201 or equivalent</td>
<td>Gloss on one side</td>
</tr>
</tbody>
</table>

3.2.2 System B

The System B material was a HexPly 6376 unidirectional carbon fibre/epoxy, received as uncured prepreg which was then laminated on-site. Four laminates at different states of cure were produced in order to investigate the effect of degree of cure on the glass transition temperature. The laminates were each made up of 16 plies and cured in an autoclave at 700 kN/m² pressure, where they were heated at 3 K/min and held for two hours at either 150°C, 160°C, 170°C or 180°C. The panels were 300 mm x 300 mm in area and 2 mm thick. The System B test specimens were dried for seven days at 80°C and stored in a controlled environment at 23°C ± 2°C and 50% ± 5% relative humidity and removed from storage no more than 30 minutes prior to testing.
3.2.3 System C

System C materials were manufactured using Hexcel 8552, a commercial epoxy resin. This group of materials included a plate of neat resin as well as plates of CFRP and GFRP which were cured at different temperatures, for which the curing schedules are described in this section. These materials were used to examine the effect of fibre reinforcement on $T_g$ measurement, as well as to study the measurement of degree of cure. The System C unreinforced epoxy resin was supplied by the manufacturer as a 30 mm x 15 mm x 3.5 mm plate, which had been cured for two hours at 180°C following a ramp rate of 0.5 K/min from ambient (23°C) to 180°C.

The GFRP and CFRP panels were manufactured by the author on-site from prepreg reinforced with either five-harness satin weave carbon-fibre cloth (CFRP), or a four-harness satin weave glass-fibre cloth (GFRP). In the first stage of production, the prepreg was cut into 300 mm x 300 mm squares, as shown in Figure 3.1. These were cut using a swing arm cutting press, which is a hydraulic-powered press that is used in conjunction with a die cutter for quick and repeatable cutting out of material. The CFRP and GFRP panels were produced using 15 plies and 40 plies, respectively, in order to produce cured laminate thicknesses of 3.75 ± 0.2 mm.

![Figure 3.1 - (left) Prepreg plies ready for lay-up and (right) panels ready for autoclaving](image)
The panels were cured at Imperial College London in two separate autoclave cycles, in order to obtain panels with different degrees of cure. Figure 3.1 shows the GFRP and CFRP panels (which are under caul plates) laid out and prepared for cure in the autoclave, also pictured. In the first run, four panels each of CFRP and GFRP were cured together at 180°C, using the cure cycle shown in Figure 3.2, where the vacuum pressure was 0.2 bar and an autoclave pressure of 7 bar. The temperature was ramped at 3 K/min to an initial hold temperature of 110°C for one hour, and subsequently raised to 180°C at 3 K/min and held for two hours, following the manufacturer’s recommendations.

The second set of GFRP and CFRP panels were cured together using the same ramp rates and pressures given by the prepreg manufacturer, but held at 145°C instead of the recommended 180°C cure temperature. This temperature was chosen through DSC trials in which samples of the GFRP and CFRP prepreg were heated in the DSC using the prepreg manufacturer recommended cure profile shown in Figure 3.2, using an upper temperature of either 145°C, 150°C or 160°C as opposed to the recommended 180°C. As part of the same run, specimens were cooled to 30°C before being subjected to a second heat ramp at 5°C to a final temperature of 300°C. From this second heat ramp, the heat of reaction was measured and used to quantify the degree of cure. This method for measuring the degree of cure is described in more detail in Section 3.3.3, and was supported by the resin manufacturer. The results of these tests are shown in Table 3.2, which indicate that a 145°C cure temperature would produce panels with a 70% degree of cure. Table 3.3 shows a summary of the fibre architecture and layup of the three materials. Fibre volume fraction measurements were obtained via acid digestion. The degree of cure of the panels cured at 145°C is given in Table 3.4

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>Degree of Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GFRP</td>
</tr>
<tr>
<td>145</td>
<td>74%</td>
</tr>
<tr>
<td>150</td>
<td>77%</td>
</tr>
<tr>
<td>160</td>
<td>81%</td>
</tr>
</tbody>
</table>

Table 3.2 – Degree of cure achieved in specimens of System C material cured at different temperatures in the DSC
Figure 3.2 – Schematic showing the autoclave cure profile of the System C material cured at 180°C and 145°C

<table>
<thead>
<tr>
<th>Resin</th>
<th>CFRP</th>
<th>GFRP</th>
<th>Neat Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre</td>
<td>HexForce AGP 280-5H (5 harness satin)</td>
<td>HexForce 220 fibre glass fabric (4 harness satin)</td>
<td>N/A</td>
</tr>
<tr>
<td>Cured plate thickness</td>
<td>3.75 ± 0.2 mm</td>
<td>3.75 ± 0.2 mm</td>
<td>3.6 ± 0.5 mm</td>
</tr>
<tr>
<td>No. plies per panel</td>
<td>15</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>Fibre volume fraction</td>
<td>69%</td>
<td>45%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.4 – Degree of cure achieved in CFRP and GFRP specimens of the System C materials cured in an autoclave at 145°C

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Cure Temp</th>
<th>Storage</th>
<th>Degree of Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>145°C</td>
<td>Ambient</td>
<td>87.4%</td>
</tr>
<tr>
<td>Carbon</td>
<td>145°C</td>
<td>Ambient</td>
<td>89.5%</td>
</tr>
</tbody>
</table>
Following autoclave cure, the undercured material which had been cured to a maximum temperature of 145°C was postcured at four different temperatures for use in the studies of the thermal analysis of cure presented in Chapter 7. The panels were cut to the desired specimen dimensions for DMA, TMA, and ILS (the sizes of the specimens are given in Section 3.3) and the resulting specimens postcured for two hours in an oven at either 155°C, 165°C, 175°C or 185°C, in order to achieve specimens at varying degrees of final cure. These specimens were then moved directly from the oven to a desiccator and stored under a controlled environment of 23°C ± 2°C, in order to prevent moisture absorption which could influence T_g measurements. The DSC and FTIR specimens were cut from the DMA-sized specimens after post-cure.

In order to study the effect of specimen storage conditions on the measurement of T_g, specimens of the GFRP and CFRP which were fully cured at 180°C in the autoclave were stored under two different conditions for comparison. One set of specimens were tested in the as-received condition and stored at room temperature and humidity, which was not controlled; this is referred to as ambient conditions throughout the remainder of the thesis. The second set of specimens were cut to the desired dimensions for testing, and dried following guidance outlined in ASTM D5229 (77). Specimens were dried at 80°C and three from each batch were weighed daily until the weight remained unchanged for three consecutive days, which was taken to be moisture equilibrium as defined by the test standard. Table 3.5 shows the changes in weight for the chosen specimens of each type, where the percentage change in weight was higher in the GFRP than the CFRP. Following the drying procedure, specimens were kept in a desiccator which was stored inside a specimen conditioning chamber held at constant temperature and humidity. Specimens were weighed on each day of testing to ensure there had been no additional moisture uptake and were not removed from the desiccator for longer than 30 minutes prior to testing. DSC specimens were taken from DMA-sized specimens which had been dried. DSC studies of the panels which were cured at 180°C show that drying of the specimens at 80°C did not significantly advance the degree of cure, as seen in Table 3.6. TMA specimens were 10 mm x 10 mm (l x w) and DMA specimens were 35 mm x 10 mm (l x w) as noted later in Sections 3.3.1 and 3.3.2. Specimens were dried for a total of 43 days.
Table 3.5 – Weight changes during drying of TMA and DMA specimens of the System C CFRP and GFRP materials (in preparation for TMA and DMA testing)

<table>
<thead>
<tr>
<th>Test Specimen Type</th>
<th>Initial Weight (g)</th>
<th>Final Weight (g)</th>
<th>% Weight Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFRP TMA</td>
<td>0.7101</td>
<td>0.7083</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.6646</td>
<td>0.6631</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>0.7325</td>
<td>0.7308</td>
<td>0.23</td>
</tr>
<tr>
<td>DMA</td>
<td>2.3981</td>
<td>2.3931</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>2.4452</td>
<td>2.4403</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>2.5871</td>
<td>2.5816</td>
<td>0.21</td>
</tr>
<tr>
<td>CFRP TMA</td>
<td>0.8907</td>
<td>0.8897</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>0.8017</td>
<td>0.8007</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.7729</td>
<td>0.7718</td>
<td>0.14</td>
</tr>
<tr>
<td>DMA</td>
<td>2.1940</td>
<td>2.1914</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>2.0726</td>
<td>2.0705</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>2.2779</td>
<td>2.2752</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 3.6 – Comparison of the degree of cure of the System C GFRP and CFRP materials after drying at 80°C for 43 days

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Cure Temp</th>
<th>Storage</th>
<th>Degree of Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>180°C</td>
<td>Ambient</td>
<td>97.5%</td>
</tr>
<tr>
<td>Glass</td>
<td>180°C</td>
<td>Dried at 80°C for 43 days</td>
<td>97.7%</td>
</tr>
<tr>
<td>Carbon</td>
<td>180°C</td>
<td>Ambient</td>
<td>99.9%</td>
</tr>
<tr>
<td>Carbon</td>
<td>180°C</td>
<td>Dried at 80°C for 43 days</td>
<td>99.9%</td>
</tr>
</tbody>
</table>
3.2.4 System D

System D materials were GFRP and CFRP manufactured in-house as part of the ongoing work at the National Physical Laboratory. These materials were fabricated from dry fabrics and infused with the same epoxy resin matrix, Gurit Prime 20LV. The GFRP reinforcement was a Formax 0/-45/90/+45 E-glass stitched cloth and the panels were manufactured by vacuum infusion. The CFRP was reinforced with a 0/90 Formax z-stitched carbon fibre fabric. Both the GFRP and CFRP panels were cured at room temperature for 24 hours and postcured at 65°C for seven hours. The finished panels were 400 mm x 400 mm x 25 mm. A cylindrical block of neat resin, dimensions 150 mm diameter x 2 mm thickness, was also cast, following the same cure profile of 24 hours at room temperature and seven hours postcure at 65°C.

3.2.5 System E

System E materials were a GFRP and CFRP manufactured in-house as part of the ongoing work at the National Physical Laboratory, as with the System D materials. The same polyester resin, Scott Bader Crystic 701PAX, was used for both the CFRP and GFRP. The GFRP was reinforced with a Formax 0/-45/90/+45 E-glass stitched cloth and the CFRP was reinforced with Formax z-stitched carbon fibre fabric. The panel was cured at room temperature for 24 hours and postcured for three hours at 80°C. The finished panels were 400 mm x 400 mm x 25 mm. In addition to the composites, a neat resin block of dimensions 150 mm diameter x 2 mm thickness was produced following the same cure profile.

3.3 Thermal Analysis Methods

Three thermal analysis techniques were used to measure the glass transition temperature of the materials studied. These were DMA, TMA and DSC. DSC was also used to measure the degree of cure of the materials. Full details of the theory behind these techniques were presented in Sections 2.5.2 (DMA), 2.5.3 (TMA) and 2.5.4 (DSC).
In addition to these thermal analysis techniques, a preliminary study was carried out using FTIR in order to assess its potential as a method for measuring the degree of cure. The next section outlines the details of sample dimensions and instrument operation for each measurement technique used.

3.3.1 DMA

The dynamic mechanical analysis in this study was performed using a TA Instruments Q800 DMA in a single-cantilever, controlled strain mode, pictured in Figure 3.5. When using this method, the DMA measures changes in the load required to subject specimens to a fixed periodic displacement during a controlled heating profile. The resulting stress, strain and complex modulus are derived by the instrument software. The Q800 instrument employs an optical encoder to measure the displacement (which the instrument software converts to strain) throughout the test.

As described earlier, specimens tested were 10 mm x 35 mm (w x l) with different thicknesses in the range 0.25 – 4 mm; specimens were tested using a single cantilever beam configuration with 0° fibres (in specimens manufactured using unidirectional or woven fibres) parallel to the length of the specimen. The machine was calibrated in accordance with the manufacturer’s guidelines prior to use.

![Figure 3.5 – Photograph of the DMA clamps which hold the specimen in the single cantilever formation inside the furnace](image-url)
Specimens used in the DMA tests were cut to dimensions 35 mm x 10 mm using a diamond circular saw. Specimens were mounted in the DMA aligned perpendicular to, and centrally within, the clamps and as close as possible to the thermocouple without allowing the sample and thermocouple to touch, as specified in ISO 6721-11. This was to obtain a temperature measured close to the sample.

Specimens were heated at a rate of 3, 5 or 10 K/min from a controlled laboratory temperature of 23°C to a final temperature of 180°C for System A, 250°C for System B and 300°C for System C. The System D and System E materials were heated to a final temperature of 180°C. The final test temperatures for each material were selected based on the $T_g$ measurement obtained from an initial test in which a specimen was heated at a ramp rate of 10 K/min to a final test temperature of 350°C, or lower if the test temperature had clearly passed through the specimen $T_g$. The final temperature selected for the subsequent runs was set to at least 50°C above the nominal $T_g$ of the material, as specified in ISO 6721-11 (65). A frequency of 1 Hz and oscillation amplitude of 10 µm were used, and tests were carried out in static air.

The measured glass transition temperature was plotted against heating rate and the results extrapolated in order to determine the $T_g$ for zero heating rate, $T_g(0)$, following the standard ISO 6721-11. In addition, the heating rate dependence for each material system was determined from the slope of the data in each case. Between tests, the instrument was allowed to fully cool to room temperature. The results of each run were analysed using the TA Instruments Universal Analysis software.

3.3.2 TMA

The TMA data included was obtained using a TA Instruments Q400 thermomechanical analyser in expansion mode. The TMA specimens of dimensions 10 mm x 10 mm were prepared using a diamond circular saw. These were tested in the through-thickness direction, where specimen thickness ranged from 0.25-4 mm (see Section 3.2 for individual material thicknesses).

The instrument was calibrated according to the manufacturer’s specifications. Specimens were placed on the sample stage and aligned within the TMA as close
to the thermocouple as possible without making contact, a distance of approximately 1 mm. The specimen placement on the sample stage is shown in Figure 3.6, with the instrument probe placed on a CFRP specimen. In this image the thermocouple is shown approximately 1 mm to the right of the CFRP specimen. Specimens were tested using a preload force of 0.05 N applied by the instrument, which ensures good contact between the probe and the specimen. In addition to the 0.05 N preload force, for TMA measurements of the System C material a 20 g mass was placed in the instrument weight tray, which applies a downward force on the measurement probe. This was used to further enhance the sensitivity to dimension changes. At the start of each TMA test, the temperature was equilibrated at 30°C prior to heating. Specimens were then heated to 250°C at a rate of 3, 5 or 10 K/min for System A and B materials and 1, 3, or 5 K/min for System C materials, where different heating rates were used in later tests of the System C materials as part of the refined test methods. The results were then extrapolated in order to find $T_g(0)$ following the method described in 2.5.2 for DMA measurement using the multiple heating rate method outlined in DMA test standard ISO 6721-11 (65).

Figure 3.6 – Photograph illustrating the placement of a CFRP specimen on the sample stage of the TMA, with the measurement probe resting on top

During the test, the linear movement of a probe located on the specimen, as pictured in Figure 3.6, was used to measure the dimension change via an LVDT; when the expansion is plotted against temperature, the glass transition temperature is identified as a point within this transition region as described in Section 2.6.3.
Following the analysis method outlined in ISO 11359-2:1999 (78), the glass transition temperature was taken as the midpoint of the transition region, using the first derivative of the dimension change with temperature as a means of indicating the limits of the transition. In order to identify the \( T_g \), the major dimension change, and the onset and end of this major change were identified with the aid of the derivative. Further details of the data analysis methods are given in the results and discussion in Chapter 5.

In between each test, the instrument was allowed to cool to room temperature. During tests which required the same specimen to undergo the temperature profile twice, no more than two hours was left between the end of the first test and the commencement of the second. The furnace was opened in between these runs to allow the instrument to cool. The results were analysed using the TA Instruments Universal Analysis software.

3.3.3 DSC

DSC was used to measure both the glass transition temperature and the degree of cure of specimens, for which the background theory is described in Section 2.6.4. The DSC measurements were made using a TA Instruments Q2000. Cured composite specimens were cut to approximately 2 mm x 2 mm x 3 mm to fit the TA Instruments Tzero aluminium crucibles and smoothed on one face using wet and dry paper to optimize contact with the base of the crucible, and therefore with the thermocouple. Figure 3.7 shows a CFRP specimen in the crucible prior to placement of the lid. Uncured prepreg specimens were similarly cut to 2 mm x 2 mm squares. Materials below 1 mm thickness were punched into discs using a sample punch.

![Figure 3.7](image)

**Figure 3.7 – Photograph showing a CFRP DSC specimen inside a Tzero aluminium crucible before the lid is put on. The specimen was cut by hand using a saw**
The instrument was calibrated using an indium temperature reference standard (NIST 2232) as part of the regular testing carried out at the National Physical Laboratory. A nitrogen gas at a flow rate of 50 ml/min was used in every test. The \( T_g \) was observed as a drop in the heat flow to the specimen as it undergoes a change in heat capacity, as described in Section 2.6.4. In order to measure the \( T_g \), specimens were heated from 30°C to 250°C using a heating rate of 5, 10 or 20 K/min. Higher heating rates than those used for DMA and TMA were used, following guidance set out in ISO 11357-2:2014 for measurement of \( T_g \) by DSC (79), owing to the higher sensitivity of the DSC to the \( T_g \) at faster heating rates. The TA Instruments Universal Analysis software was used to process the results. The \( T_g \) was taken as the inflection point of the heat flow curve and, again, the thermal lag approach was adopted to find \( T_g(0) \) in order to study the effect of thermal lag on DSC measurements.

Following ISO 14322:2012 (80), the degree of cure was measured using the exothermic peak in the DSC measurement of heat flow. The uncured prepreg was heated at 5 K/min to 350°C to obtain the total heat of reaction. The degree of cure of the material was calculated using Equation 3.1 and two specimens were used to check for reproducibility.

\[
\text{Degree of cure (\%)} = \left(1 - \frac{H_S}{H_T}\right) \times 100 \quad (3.1)
\]

where, \( H_S \) is the heat of reaction of the specimen being assessed and \( H_T \) is the total heat of reaction obtained from measurements performed on the uncured prepreg.

3.3.4 FTIR

Fourier transform infrared spectroscopy (FTIR) was used as a means of assessing the degree of cure of the composite materials. The method was based on a new draft standard. FTIR was carried out using a ThermoScientific Nicolet iS50 FT-IR in ATR mode.
3.4 Concluding remarks

In this chapter, the experimental methods were described, covering material manufacture and measurement techniques. In the next few chapters, the experimental results for each test method are presented and discussed, beginning with DMA.
4 DMA measurement of $T_g$

4.1 Introduction

In the review of the literature it was shown that the glass transition temperature, $T_g$, can not only provide information on service temperature, but can also be related to changes in the degree of cure of polymer composites. Dynamic mechanical analysis (DMA) is a thermal analysis technique which offers a high sensitivity to the glass transition, making it one of the most common methods used in both industry and academia. One of the major drawbacks of this technique is the impact of thermal lag, in which the temperature of the specimen takes longer to increase than the instrument thermocouple. This causes an artificially high $T_g$ to be recorded and thus hamper the precision of data obtained. Thermal lag between the specimen and the furnace has been the subject of a number of studies, both experimentally and through numerical modelling, as previously discussed in the literature review in Chapter 2 (37, 38, 42, 46, 62, 66, 67).

In this chapter, measurement of the $T_g$ of polymer matrix composites by DMA has been studied using a recent test method, outlined in test standard ISO 6721-11, in which different specimens are tested at a range of heating rates. This method has been used to study experimentally how the effect of thermal lag can be compensated to enable more precise measurement of $T_g$ by DMA. In addition, the effect of changing specimen thickness, fibre reinforcement and moisture levels on the measurement of $T_g$ has been studied. To supplement the experimental data, CoDA software has been used to model the diffusion of heat through a DMA specimen and compared for different specimen thicknesses.

4.2 The “multiple heating rate” method for measuring $T_g$

The experimental procedure and analysis methods used in DMA testing can vary from user to user and laboratory to laboratory. This section introduces the “multiple heating rate” method, following guidance in test standard ISO 6721-11 (65), which has been used throughout this chapter. As outlined in the previous chapter, in this
method, separate specimens are tested at different heating rates, using a new specimen of the same material for each test. The results are then plotted on a graph of $T_g$ against heating rate in order to extrapolate the value for $T_g$ at zero heating rate, known as $T_g(0)$. In the work presented in this chapter, heating rates of 3, 5 and 10 K/min were used.

Figure 4.1: DMA data for 3.5mm thick CFRP tested at 5 K/min

During analysis of DMA data, there a number of analysis points that can be identified as the $T_g$, as previously described in Section 2.5.2. A representative graph of the data output from the DMA is presented in Figure 4.1. The figure shows the graphs of the storage modulus (shown in green), loss modulus (shown in blue) and tan delta (shown in red), plotted against temperature. This graph shows the response of a 3.5 mm thick carbon fibre reinforced epoxy specimen (System A), 35 mm x 10 mm (length x width), prepared using the method outlined in Section 3.3.1. The specimen was heated from the controlled laboratory atmosphere of 23°C to 180°C at a heating rate of 5 K/min, using a displacement oscillation amplitude of 10 µm in the single cantilever formation. In the resulting graph in Figure 4.1, the glass transition region can be identified from the clear change in each of the signals, in the region between 70°C to 100°C. This is seen in the storage modulus as a defined drop, from which the inflection point (in this case 78.4°C as seen on the graph) is
typically taken as the $T_g$. Alternatively, the $T_g$ can be interpreted as the peak of either the loss modulus or the tan delta seen in the same temperature region, which for this specimen are 79.4°C and 82.9°C, respectively, as shown in the figure. For these commonly used measurements of $T_g$, there is a variation of approximately 4°C between the highest value, the tan delta peak, and the lowest value, the storage modulus inflection point. This provides a good example of the need for standardisation work due to the complexity of $T_g$ measurement which can vary greatly between common DMA analysis points using the same equipment.

The TA Universal Analysis 2000 software can automatically calculate the onset, inflection and end point values, within user-defined limits, as was used to locate the specific analysis points identified in Figure 4.1. Identification of the loss modulus and tan delta peaks as carried out by the software can be considered conclusive, as this analysis simply relies on finding the highest point of the peak. Location of the inflection point of the storage modulus, however, involves a procedure that could be considered more subjective, as it relies on tangent lines (produced by the software) drawn between two limits (set by the user). In order to assess the validity of the software-calculated values, the computed outputs for three identical tests (the test for which the data was presented in Figure 4.1 and two repeats) were compared to values for the inflection point calculated by hand from the raw data. The results are given in Table 4.1. The largest difference between the computed values and hand calculated values for the inflection point of the graph of the storage modulus was 0.4°C, which can be considered acceptable.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Software (°C)</th>
<th>Calculated (°C)</th>
<th>Difference (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>86</td>
<td>85.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>79</td>
<td>79.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Specimen 3</td>
<td>74</td>
<td>74.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>
In the next stage, samples of the 3.5 mm thick System A CFRP panel were tested in the DMA, heated from the controlled laboratory temperature (23°C) to 180°C, at different heating rates. In addition to the data collected in the previous test at 5 K/min, heating rates of 3 and 10 K/min were used. The changes in storage modulus, loss modulus and tan delta with heating rate are presented in Figure 4.2, Figure 4.3 and Figure 4.4, respectively, where the data from the test presented in Figure 4.1, on the same material (tested at 5 K/min), has been included. From the graphs a shift in the glass transition temperature towards higher temperatures with increasing heating rate can be observed; this is shown by the arrows in each of the figures. This shift highlights the heating rate dependence on the measured value of the glass transition temperature for this material.

![Graph showing variation in storage modulus with heating rate during DMA of 3.5mm CFRP](image)

**Figure 4.2: Variation in storage modulus with heating rate during DMA of 3.5mm CFRP**
Figure 4.3: Variation in loss modulus data with heating rate during DMA test on 3.5mm CFRP

Figure 4.4: Variation in tan delta with heating rate during DMA of 3.5 mm CFRP
The storage modulus inflection point, the peak of the loss modulus and the peak of the tan delta, which are usual measures of $T_g$, have been plotted against heating rate in the graphs in Figures 4.5, 4.6 and 4.7, for the data obtained at each of the three heating rates. Each test at the three different heating rates was repeated three times (using new specimens of the same material for each test) and all of the results are plotted on the graphs. The results show that the maximum variation in $T_g$ between the lowest and highest heating rates used was about 11°C for the storage modulus, loss modulus and tan delta. From these three figures it is clear that the heating rate used can cause large differences in the measured $T_g$ values, regardless of which analysis point is used to identify the $T_g$. As $T_g$ is a value used for the qualification of composite materials, these results show the importance of understanding the effect of test procedure on the resulting measured values, which could be the difference between a pass or fail of a material or component during quality assurance testing. The multiple heating rate method has been used for all DMA tests which follow, including studies of how the heating rate dependence is affected by material type, preparation and thickness.

![Graph of heating rate against storage modulus inflection point for the 3.5 mm thick System A CFRP](image)

**Figure 4.5:** Graph of heating rate against storage modulus inflection point for the 3.5 mm thick System A CFRP
Figure 4.6: Graph of heating rate against loss modulus peak for the 3.5 mm thick System A CFRP

Figure 4.7: Graph of heating rate against tan delta peak for the 3.5 mm thick System A CFRP

The gradients of the fit lines shown in Figure 4.5, Figure 4.6 and Figure 4.7, described in the standard as the calibration curve, and the point of intersection at zero heating rate, known as $T_g(0)$ are given in Table 4.2 for each of the three analysis points (the storage modulus inflection point, peak of the loss modulus and the peak of the tan delta). The gradients are a measure of the heating rate dependence of
the $T_g$. The data given in Table 4.2 shows that the peak of the tan delta offers the highest measured $T_g$ value, which confirms previous observations in the literature (39, 42). While the tan delta can be useful for providing information on a material’s damping properties, the recent test standard ISO 6721-11 recommends the use of the storage modulus inflection point or the peak of the loss modulus for determining the glass transition temperature. These three analysis points are examined further in the next section.

Table 4.2: $T_g(0)$ and heating rate dependence taken from the graphs of the storage modulus, loss modulus and tan delta against temperature for DMA measurements of 3.5 mm CFRP

<table>
<thead>
<tr>
<th></th>
<th>$T_g(0)$ (°C)</th>
<th>Gradient (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage Modulus (Inflection Point)</td>
<td>72.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Loss Modulus (Peak)</td>
<td>72.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Tan Delta (Peak)</td>
<td>75.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

4.3 Effect of Specimen Thickness

The previous section introduced the effect of changing the heating rate on $T_g$ measurement, showing that faster heating rates lead to an increase in measured $T_g$. This occurs as a result of an increase in thermal lag between the internal temperature of the specimen and the temperature measured by the instrument thermocouple, which is close to the specimen surface. As a consequence, it appears likely that the thickness of the specimen must also have an association with thermal lag and the heating rate dependence of the $T_g$. To investigate this relationship, tests were carried out on specimens of different thicknesses from the System A materials using the multiple heating rate method. These were the woven CFRP specimens of thicknesses 0.25 mm, 0.5 mm, 1 mm, 2 mm, and 3.5 mm described in Chapter 3.

The measured $T_g$ values have been plotted against heating rate in Figures 4.8 (a-e) for each specimen thickness. Each graph shows the values for the storage modulus inflection point, the peak of the loss modulus, and the peak of the tan delta.
The data show, again, that the storage modulus inflection point and the loss modulus give lower values of $T_g(0)$ than the tan delta. These differences in $T_g(0)$ between the three analysis points have previously been reported in the literature, however to the author’s knowledge these comparisons have not been made for tests at different thicknesses (42, 59, 81). These data show that the same values of $T_g(0)$ taken from the storage and loss moduli were obtained for specimen thicknesses of 1 mm and above. However, for specimen thicknesses below 1 mm, or more specifically 0.25 mm and 0.5 mm, significant signal noise impacted the quality of the data, therefore demonstrating that the DMA testing in this mode (flexure) is not suitable for these specimen thicknesses. In subsequent analyses, only the storage modulus inflection point, as recommended in ISO 6721-11, was plotted against other test parameters.
(b) 0.5 mm

Heating Rate (K/min)

(c) 1 mm

Heating Rate (K/min)
Figure 4.8 (a-e): New procedure using multiple heating rates applied to Tg measurement by DMA for specimens of thicknesses a) 0.25 mm b) 0.5 mm c) 1 mm d) 2mm and e) 3.5 mm
The gradients of the graphs in Figure 4.8 (a-e) have been plotted against specimen thickness in Figure 4.9 for each of the three analysis points, showing the relationship between heating rate dependence (and consequently thermal lag) and specimen thickness. The data show that the heating rate dependence increases with specimen thickness. The specimen of 0.25 mm thickness did not seem to follow the trend closely; however, as previously stated, significant signal noise was seen in the data for these thinner specimens due to their much lower flexural stiffness and the low loads created. DMA testing in tension or torsion could be superior to testing in flexure and give more consistent data for specimens of this lesser thickness.

Figure 4.9 suggests a potential normalization of data for different thicknesses.

**Figure 4.9:** Graph of the heating rate dependence against specimen thickness for DMA of Series A CFRP using (a) storage modulus inflection point; (b) loss modulus peak and (c) tan delta peak as a measure of Tg. Data points with brackets [ ] are considered unreliable.

In Figure 4.10, the storage modulus inflection point data for the five different specimen thicknesses (of the System A material) have been compared on the same graph, offering further information on both the material and the thermal lag effect. When compared, the $T_{g(0)}$ for the different thicknesses of material can clearly be separated into values of 112-125°C for the 1 mm and 2 mm material, and 70-85°C for the 0.25 mm, 0.5 mm and 3.5 mm material. In order to verify this observation, the $T_g$ of these materials was measured using DSC and TMA (excluding the 0.25
mm and 0.5 mm thick material), with the results shown in Table 4.3. This notable difference in \( T_g(0) \) is great enough to be of major concern to end users and product design when it is considered that these materials had been described as nominally identical – albeit of different thicknesses – by the supplier. One explanation for this difference in \( T_g \) could be that different resin systems were used. Whilst the resin was listed as ‘SGL CE1201 or equivalent’ by the material supplier, the \( T_g \) values of the materials are not comparable. It is worth noting that the three thicknesses of material with a higher glass transition temperature all had a smooth, glossy finish on one side of the plate, which can typically be attributed to the effects of curing a panel on a caul plate covered by a release film. The 1 mm and 2 mm materials were textured (due to the fabric) on both sides. This difference in finish between the materials could be an indicator of two different processing methods or manufacturers. Design with the data from the 1 mm and 2 mm thick specimens would probably fail in service if constructed from the 3.5 mm thick material.

![Graph of inflection point against heating rate for DMA of Series A CFRP showing effect of specimen thickness on Tg measurement](image)

**Figure 4.10**: Graph of inflection point against heating rate for DMA of Series A CFRP showing effect of specimen thickness on \( T_g \) measurement
Table 4.3: Comparison of $T_{g(0)}$ values for System A materials by DMA, TMA and DSC, where the specimens with a $T_g$ in a different temperature region are highlighted in grey

<table>
<thead>
<tr>
<th>Specimen Thickness</th>
<th>$T_{g(0)}$ DMA</th>
<th>$T_{g(0)}$ TMA</th>
<th>$T_{g(0)}$ DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 mm</td>
<td>75.6</td>
<td>Too thin for test</td>
<td>62.5</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>79.4</td>
<td>Too thin for test</td>
<td>65.0</td>
</tr>
<tr>
<td>1 mm</td>
<td>113.5</td>
<td>107.2</td>
<td>103.4</td>
</tr>
<tr>
<td>2 mm</td>
<td>113.1</td>
<td>97.1</td>
<td>106.5</td>
</tr>
<tr>
<td>3.5 mm</td>
<td>72.0</td>
<td>63.4</td>
<td>66.2</td>
</tr>
</tbody>
</table>

The trend observed in Figure 4.9, in which the results fall onto one line despite any differences in $T_g$, indicates that the heating rate dependence occurs as a consequence of the thermal lag in the test, which is related to the thermophysical properties of the specimen and not the $T_g$, which is a property of the matrix resin only. The thermal lag effect is expected to be dependent on the material diffusivity due to the dynamic conditions under which DMA specimens are tested. The important physical feature in this test is the rate at which heat permeates through the material.

In order to further study the relationship between specimen thickness and heating rate dependence, specimens of both GFRP and CFRP from the System C material were machined to different thicknesses varying from 0.5 mm to 3.5 mm using a diamond face grinder. These specimens were all obtained from the same respective panel (either GFRP or CFRP) in order to ensure that they had experienced the same cure conditions. Following machining, the specimens were dried in an oven at 80°C for one week to minimise the effects of any variation in moisture content between the different specimen types. Two specimens of each thickness and material were tested at each heating rate of 3, 5 and 10 K/min. The graph in Figure 4.11 demonstrates that, while the gradient of the heating rate dependence increases with specimen thickness, as expected, the absolute values differ for each material. Interestingly, there is a large difference between the heating rate dependences for the System C GFRP and CFRP, which were composed of the same matrix resin,
varying only in reinforcement type. This indicates that the type of reinforcement used is an important factor in the relationship between specimen thickness and heating rate dependence.

![Graph of heating rate dependence (gradient) against thickness for CFRP and GFRP specimens from System A and System C](image)

**Figure 4.11:** Graph of heating rate dependence (gradient) against thickness for CFRP and GFRP specimens from System A and System C

### 4.4 Effect of reinforcement and matrix material choice

The glass transition temperature is a property measured when the matrix resin of a polymer matrix composite changes from the glassy to the rubbery state, or vice versa. In this section, the effect that the fibre reinforcement can have on the overall \( T_g \) of the composite material, as well as the effect of the fibres on heating rate dependence, has been investigated.

The glass transition temperature of each of the three System C materials; (i.e. GFRP, CFRP and neat resin), was measured by DMA using the multiple heating rate method, using heating rates of 3, 5 and 10 K/min and the results are shown in Figure 4.12. The comparison of these three System C materials shows that the \( T_g^{(0)} \) values are very similar, with only quite small heating rate differences. It was reported by Terpilowski et al. (82) that the thermal diffusivity of CFRP is higher than that of GFRP, therefore it would be anticipated that thermal lag in the CFRP specimens would be reduced, resulting in a lower heating rate dependence. However, as noted
in Good Practice Guide GPG62 (83), a higher heating rate dependence was observed in specimens made with higher thermal conductivity materials, which may be attributable to detailed material/equipment interactions, such as heat losses through the clamp/oscillator systems.

![Graph of T_g against heating rate for 3.75 mm thick Series C materials tested by DMA](image)

**Figure 4.12:** Graph of $T_g$ against heating rate for 3.75 mm thick Series C materials tested by DMA

The thermal conductivities of the System C GFRP and CFRP materials were measured using the guarded hot plate system described by Stacey et al. (84), as part of the routine measurement service provided by the National Physical Laboratory. A circular specimen of each material, of diameter 50 mm and thickness 3 mm, was tested at five temperatures; 50°C, 100°C, 150°C, 200°C and 250°C. The CFRP specimen was cycled through each of the five temperatures a second time, however no significant difference in the thermal resistance was found between the results of the two test runs. The results of the CFRP tests are shown in Figure 4.13. The thermal resistance of the GFRP, on the other hand, was found to increase between the first and second test run, and so the test was repeated a total of five times, where a small increase in thermal resistance was found each time. This occurred as a result of the incomplete cure of the GFRP material when compared with the CFRP material. The cure temperature used during the manufacture of this material was 180°C, which was exceeded by the maximum test temperature of the
thermal resistance tests. This advanced the degree of cure with each test run, which was reflected in a visible darkening of the GFRP specimen at each stage. Figure 4.14 shows that this in turn resulted in an increase in thermal resistance, although the total change was less than 4% while the measurement uncertainty was 7.5%.

Figure 4.13 – Graph of the thermal resistance of the System C CFRP measured in the guarded hot plate

Figure 4.14 - Graph of the thermal resistance of the System C GFRP measured in the guarded hot plate, showing data for the same specimen tested five times
The values of thermal resistance and thermal conductivity between the GFRP and CFRP have been compared in Table 4.4, where only the values from the first test run have been presented as they reflect the “as received” state of the material when tested by DMA (Figure 4.12). The table shows that a difference of 70-86 KWm\(^{-2}\) in the thermal conductivity was found between the two materials at each temperature. This replicates the findings of Terpilowski et al. (82) in which the thermal conductivity of the CFRP was found to be higher, which would be expected to result in a lower thermal lag for the DMA tests of the CFRP. This is discussed further below.

<table>
<thead>
<tr>
<th>Test Temperature (°C)</th>
<th>Thermal resistance (\text{m}^2\text{KW}^{-1})</th>
<th>Thermal conductivity (KWm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GFRP</td>
<td>CFRP</td>
</tr>
<tr>
<td>50</td>
<td>0.0080</td>
<td>0.0051</td>
</tr>
<tr>
<td>100</td>
<td>0.0078</td>
<td>0.0048</td>
</tr>
<tr>
<td>150</td>
<td>0.0077</td>
<td>0.0047</td>
</tr>
<tr>
<td>200</td>
<td>0.0080</td>
<td>0.0047</td>
</tr>
<tr>
<td>250</td>
<td>0.0089</td>
<td>0.0052</td>
</tr>
</tbody>
</table>

In order to understand whether the effects seen in the System C material would be the same for other polymer matrix composites or are inherent to the epoxy resin used, the DMA test was repeated with a further two resin systems; an alternative epoxy system (System D) and a polyester resin (System E). Both resin systems were used to produce carbon fibre and glass fibre reinforced composite materials as well as specimens of the neat resin. Details of the manufacture of these materials are given in Chapter 3. The results of these tests are shown in Figures 4.15 and 4.16 for the epoxy-based and polyester-based composites, respectively. As is shown in the data, the relationship between the \(T_g\) values for each of the three reinforcements (or neat resin) follows the same trend as that for the System C materials, specifically that there is little difference between the \(T_g\) values. The one exception is that the CFRP materials exhibit a slightly higher heating rate dependence than the GFRP and neat resin.
Figure 4.15: Graph of $T_g$ against heating rate for System D materials measured by DMA

Figure 4.16: Graph of $T_g$ against heating rate for System E materials measured by DMA
4.5 Specimen Conditioning

It is known that moisture absorption can affect the $T_g$ of a polymer matrix composite (85). It is common practice to dry specimens prior to testing for industry qualification purposes, and it would be useful to understand and quantify the effect that this has on the heating rate dependences discussed above. Figure 4.17 shows the measured $T_g$ values of the System C CFRP and GFRP specimens for two conditions. In the first case, specimens have been stored under ambient conditions, i.e. uncontrolled room temperature and humidity; in the second case, specimens were dried at 80°C following ASTM D5229 (77) and stored in a desiccator under a controlled room temperature of $23°C ± 2°C$, as described in Section 3.2.3.

![Figure 4.17: Comparison of $T_g$ of GFRP, CFRP and neat resin in two different moisture conditions as measured by DMA at a range of heating rates](image)

The plots of $T_g$ against heating rate in Figure 4.17 for both CFRP and GFRP show that there is a rise in the glass transition temperature of 6-7°C after specimen conditioning. In spite of this change in $T_g$, the relationship between heating rate and $T_g$ remains the same for each material after drying. This indicates that the moisture uptake does not have a significant influence on the slope of the heating rate dependence.
4.6 Measurement of Heat Transfer within the DMA Furnace

4.6.1 Heat transfer within the furnace and from the furnace

The multiple heating rate method was designed to eliminate the effects of thermal lag in DMA testing. This arises from a difference between the heat transfer from the furnace to the air inside the furnace and from the air to the specimen, which is held inside the furnace by a metal clamp. It has been proposed that the degree of thermal lag can be affected by the thermal conductivity of the equipment. In particular, it has been suggested in Good Practice Guide GPG62 (83) that heat transfer out of the furnace via the specimen clamps could influence measured thermal lag, as discussed earlier (i.e. the thermal lag is not solely dependent on the material properties of the specimen).

![Graph demonstrating the impact of insulating a CFRP specimen from the metal clamps inside the furnace during a DMA test](image)

**Figure 4.18:** Graph demonstrating the impact of insulating a CFRP specimen from the metal clamps inside the furnace during a DMA test

In order to investigate this further, an experiment was carried out in which the DMA specimen was insulated from the clamps using a glass slide which was cut to size. Tests were carried out using this setup on CFRP specimens (System C) at heating rates between 3 K/min and 10 K/min. The results are plotted in Figure 4.18, together
with the data for tests carried out without insulation. The results suggest that the thermal lag effect for the CFRP specimens is slightly higher when the specimens are not insulated from the grips. In other words, in the previous set of results (Figures 4.15 and 4.16), the heating rate dependence for the CFRP specimens may possibly have been overestimated because the specimens were not insulated from the grips. If this is the case, it may resolve the apparent contradiction between the thermal conductivity results (where the CFRP has the higher thermal conductivity) and the apparently larger effect of thermal lag in the CFRP specimens compared to the GFRP specimens (when the opposite would be expected). However, for completeness, a similar experiment with GFRP specimens insulated from the grips is required to assess whether insulating GFRP specimens from the grips also affects the thermal lag.

4.6.2 Heat transfer across the specimens

Differences in heating rate dependence and thermal conductivity have been found for the GFRP and CFRP specimens, as seen in Section 4.4. Sun et al. (66) studied the difference in temperature between the specimen and furnace during DMA testing. The authors placed thermocouples at two locations inside DMA specimens in addition to a thermocouple located within the furnace, 2 mm from the instrument thermocouple. The measurements from each of these four thermocouples were compared in order to study the temperature differences measured. These tests were carried out on GFRP and epoxy specimens. The authors found the largest difference in temperature for the instrument-defined $T_g$ at the highest heating rate used, 10 K/min. Thermal lag was found to occur between the two sensors within the specimen, as well as between the instrument thermocouple and those inside the specimen.

In this section, a thermocouple was embedded within each of the specimens of the System C CFRP and GFRP and used to measure the difference between the internal temperature of the specimen and the temperature read by the instrument thermocouple (within the DMA furnace) when the specimen is subjected to a
dynamic heat ramp. This difference in temperature has then been compared for the GFRP and CFRP specimens, which were fabricated using the same matrix resin.

The study was carried out using K-type thermocouples, where the thermocouple type refers to the two types of wire used in the internal measurement configuration; in this case chromel and alumel. The thermocouple was inserted into the specimen at the centre, via a hole drilled in the centre of the specimen as depicted in the schematic diagram in Figure 4.19. The wires formed a tight fit inside the drilled hole. The thermocouple wires were led out of the furnace (when in the closed position) to the temperature logger.

The CFRP and GFRP specimens were heated from room temperature to 180°C at a rate of 3 K/min in separate runs. Figure 4.20 shows the graph of the temperature as read by the instrument thermocouple and the temperature as read by the thermocouple placed inside the GFRP specimen, plotted against time. The same comparison is shown in Figure 4.21 for the CFRP specimen. When overlaid, these plots are almost identical, which is surprising given the difference in thermal conductivities of CFRP and GFRP. The CFRP results also reproduced previously unpublished results from NPL.

![Thermocouple](image)

Figure 4.19 – Schematic showing the thermocouple placement inside a DMA specimen used to measure the internal specimen temperature
Figure 4.20: Graph of temperature against time as measured by the instrument thermocouple and a thermocouple located inside the specimen for GFRP tested at 3 K/min

Figure 4.21: Graph of temperature against time as measured by the instrument thermocouple and a thermocouple located inside the specimen for CFRP tested at 3 K/min
4.7 CoDA modelling of heat transfer

4.7.1 Introduction

CoDA is a program developed by NPL that is used for the preliminary design of composite components through modelling of the properties of composite materials and structures. In this section, the CoDA software has been used to model heat diffusion through the thickness of CFRP specimens. The diffusion through specimens of different thicknesses has been assessed and the model has been used to find a relationship between specimen thickness and the heating rate used in DMA measurements of $T_g$.

4.7.2 Modelling specimens of different thickness

The CoDA modelling software was used to model the heat transfer through specimens of different thicknesses, in order to provide an insight into the heat profile through the thickness of a specimen over time. The software uses the following equation in order to calculate the temperature profile across the thickness of the specimen at time instant, $t$:

$$T_b + \frac{(T_t - T_b)}{h} (z + h/2)$$

$$+ \sum_{j=1}^{100} \left\{ \frac{2}{j\pi} \sin \frac{j\pi (z + h/2)}{h} \exp \left[ -\kappa_{zz} t \left( \frac{j\pi}{h} \right)^2 \right] \left[ (T_t - T_i) \cos(j\pi) - (T_b - T_i) \right] \right\}$$

where $T_i$ is the initial temperature across the specimen, $T_t$ and $T_b$ are the top and bottom temperatures at the specimen surfaces, $z$ is the through-thickness distance measured from the mid-plane, $\kappa_{zz}$ is the laminate heat diffusivity coefficient in the through-thickness direction and $h$ is the laminate thickness.
It is not possible to use this software to model the dynamic heating conditions used in the DMA tests, therefore the model was based on an isothermal temperature condition. The initial specimen temperature was set to 0°C and the instantaneous surface temperature of the specimen was set to 100°C, as this is within the characteristic test temperature region for high performance composite materials. For the purposes of this study, the CFRP laminate was modelled as a [0/90] material due to difficulties in modelling of woven fabrics that result from the lack of information that is currently available (this is still a widely researched area of work and not within the scope of the thesis). The thicknesses used for the modelling were 0.25 mm, 0.5 mm, 1 mm, 2 mm and 3.5 mm and the CoDA software assumes the specimen to be of infinite length and width. The plots in Figure 4.22 (a-e) show the CoDA model of the heat profile across the five different thicknesses of specimen after a time of 0.5s. In these plots, the thickness of the specimen is plotted as the “distance from the centre” on the y-axis and the temperature is plotted on the x-axis, giving a view of the temperature gradient across the specimen. The data provided by CoDA shows that there is a significant difference between the temperature profiles of each specimen after 0.5 seconds, assuming a surface temperature of 100°C at time zero.
Using the same conditions, the CoDA software was used to predict the time taken for the heat of the surface to diffuse through the specimens so that the centre line temperature (at a distance of 0 mm on the y-axis) matched the surface temperature. The time to equilibrate the temperature across the thickness of the specimens was predicted for all specimens, assuming a surface temperature of 100°C. This time to equilibrium is plotted as a function of specimen thickness in Figure 4.23.

The graph in Figure 4.23 shows that for the 3.5 mm thick specimen, it takes 195s for the temperature at the centre of the specimen to match that of the surface. For the heating rates used in DMA, this could result in a difference of almost 10°C for a 3 K/min heating rate and over 30°C for a 10 K/min heating rate between the furnace temperature (read by the thermocouple) and the temperature at the centre of the specimen. As a check, the surface temperature at time zero was increased to 1000°C and it was found this did not significantly alter the time taken for the specimen to reach a temperature equilibrium. From the data in Figure 4.23, there is a clear relationship between the specimen thickness and time to equilibrium, in which the time, \( t \), is proportional to the square of the specimen thickness, \( h \), i.e.

\[ t \propto h^2 \]
This relationship between specimen thickness and time to equilibrium can be used to develop a relationship between the heating rates required when comparing the T\textsubscript{g} values of specimens of different thickness (for the same material) when using DMA.

Mano and Cahon (86) suggested that due to the difference between the surface and centre line temperatures of the specimen, what is described as the specimen temperature when measuring the T\textsubscript{g} is actually an average of the temperatures across the specimen. In the relationship between heating rate and specimen thickness to be developed here, it has been assumed that the specimen does not change from the glass to the rubbery state until the centre of the specimen has reached the T\textsubscript{g}; this is obviously a simplification, but enables a simple relationship to be derived. Expanding on the relationship found in Figure 4.23, if the heating rate is taken as R = x K/min, then the time, t, taken for the centre line temperature to reach the temperature of the surfaces is given by

\[ t \propto \frac{1}{R} \propto h^2 \]

Consequently

\[ \frac{1}{R} \propto h^2 = k h^2 \therefore k = \frac{1}{Rh^2} \]

It follows that for two specimens of two different thickness, h\textsubscript{1} and h\textsubscript{2}, the heating rates (R\textsubscript{1} and R\textsubscript{2}) required for the centre line temperature to equilibrate to the same surface temperature leads to the following relationship:

\[ \frac{1}{R_1 h_1^2} = k = \frac{1}{R_2 h_2^2} \]

Therefore, the heating rate, R\textsubscript{2}, for a specimen of thickness, h\textsubscript{2}, to equilibrate to the same surface temperature as a specimen of the same material of thickness, h\textsubscript{1}, tested at heating rate, R\textsubscript{1}, is found to be

\[ R_2 = R_1 \left( \frac{h_1}{h_2} \right)^2 \] \hspace{1cm} (4.1)

In practical terms, then, this equation can be used to compare different thicknesses of the same material (h\textsubscript{1} and h\textsubscript{2}), when the T\textsubscript{g} of one thickness of material (h\textsubscript{1}) has
been obtained via DMA testing at a given heating rate ($R_1$); it should be noted that the $T_{g(0)}$ does not need to be known for this comparison. The equation predicts the heating rate, $R_2$, that should be used for the specimen thickness, $h_2$ to measure the same $T_g$. This is a useful tool for comparing $T_g$ values as an alternative to the multiple heating rate method for finding the $T_{g(0)}$, where it may not always be possible to carry out multiple DMA tests to obtain the “calibration curve” used to find the $T_{g(0)}$.

The diagram in Figure 4.24 shows the relationship used in this way, schematically. A material with a certain (unknown) $T_{g(0)}$ is tested with a thickness of $h_1$ at a heating rate $R_1$, and the $T_g$ is measured to be 121°C. For a specimen of the same material with a thickness of $h_2$ to show the same value of $T_g$, the heating rate, $R_2$, is given by

$$R_2 = R_1 \left( \frac{h_1}{h_2} \right)^2$$

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![Graph](image_url)

**Figure 4.23** – Graph of the time to temperature equilibrium for specimens of different thicknesses as modelled in CoDA

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In order to validate this method against experimental data, the System A DMA data has been reproduced in Figure 4.25 from Section 4.3 for the materials of thickness 1 mm, 2 mm and 3.5 mm. As described previously, the 3.5 mm material possessed a different $T_g$ to the 1 mm and 2 mm materials. As this difference in $T_g$ was proven to not affect the trend in heating rate dependence, the data for the 3.5 mm material has been shifted to ensure the $T_g(0)$ values converge at the same point, i.e. $T_g(0) = 113^\circ$C, as this is necessary to apply Equation 1. The 1 mm, 2 mm and 3.5 mm data can now be taken as the experimentally measured data.

To compare the experiment with the predictions of Equation 1, the $T_g$ value measured for the 1 mm thick material at a heating rate of 10 K/min has been used; this was $117^\circ$C. Using equation 1, with $R_1 = 10$ K/min and $h_1 = 1$ mm, then for a specimen of thickness 2 mm ($h_2$), the heating rate necessary to obtain the same $T_g$ would be 2.5 K/min. From the experimental data in Figure 4.25, the heating rate of 2.5 K/min would give a measured $T_g$ of $115^\circ$C, which is within 2$^\circ$C of $117^\circ$C. Similarly, using the same method, for a specimen of thickness 3.5 mm, the heating
rate predicted to give the same $T_g$ would be 0.8 K/min; the experimental data shows that for this heating rate, the $T_g$ measured would have been 114°C, which is within 3°C of 117°C. Hence, a comparison of experiment and prediction shows that (4.1 is correct to within 3°C for heating rates ranging from 0.8 K/min to 10 K/min, and thicknesses between 1 mm and 3.5 mm. The comparisons are shown in Table 4.5.

![Graph of the $T_g$ against heating rate for the System A materials of different thicknesses, showing the adjustment for the 3.5 mm thick material to enable this data to be used to help validate the relationship found between heating rate and specimen thickness.](image)

**Table 4.5** – Validation of the new equation relating specimen thickness, $h$, and heating rate, $R$, for the same $T_g$ using DMA data of the System A materials

<table>
<thead>
<tr>
<th>$h$ (mm)</th>
<th>$y$</th>
<th>$R$ (K/min)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3594x + 113.47</td>
<td>10</td>
<td>117</td>
</tr>
<tr>
<td>2</td>
<td>0.9296x + 113.15</td>
<td>2.5</td>
<td>115</td>
</tr>
<tr>
<td>3.5</td>
<td>1.321x +112.96</td>
<td>0.8</td>
<td>114</td>
</tr>
</tbody>
</table>
4.8 Concluding Remarks

In this Chapter, a number of factors that can impact the precision of $T_g$ measurement by DMA have been examined. A new test procedure presented in test standard ISO 6721-11 whereby different specimens are tested at multiple heating rates was used to identify which of these factors can impact the heating rate dependence and measurement of $T_g$. The results obtained indicate that measuring the $T_g$ using the inflection point of the storage modulus measured by DMA and using the new method of testing different specimens at a range of heating rates, is the preferred method for identifying the $T_g$ of a polymer matrix composite.

The data obtained for different thicknesses of nominally identical material, suggest that the heating rate dependence of the thermal lag could be predicted using a simple relationship between heating rate and specimen thickness.

These studies have provided additional guidance on the application of the DMA technique that could be usefully incorporated in future standards, as a means to exploit the comparatively higher sensitivity of DMA whilst accounting for thermal lag effects in order to increase precision, comparability and consistency of $T_g$ measurement.
5 Alternative T\(_g\) measurement techniques (TMA and DSC)

5.1 Introduction

In the previous chapter, a number of factors that can influence the measurement of T\(_g\) by DMA were quantified and validated. In particular, a new method which uses multiple heating rates was used successfully to eliminate the effect of thermal lag on DMA results. In this chapter, this multiple heating rate method has been applied to two additional and widely-used techniques (DSC and TMA), also used for measurement of T\(_g\) as an indicator of cure, in order to assess their dependence on heating rate. As noted earlier in Chapter 3, these techniques are carried out in the same manner as the DMA by noting transitions that occur as the sample is heated at a constant ramp rate. The multiple heating rate method has been used to establish whether or not the extrapolated value, T\(_{g(0)}\) can be used to find a consistent T\(_g\) for a given material when using these techniques, which are known to give different values from each other. Other variables which can influence the measurement of T\(_g\) by TMA and DSC have also been studied, including specimen preparation, experimental setup and analysis of results.

5.2 TMA measurements of T\(_g\)

In the first series of tests using TMA, the technique was used to measure the T\(_g\) of specimens of the System A CFRP, which varied in thickness from 0.25 mm to 3.5 mm. The aim of the study was to examine the effect of specimen thickness on the measured T\(_g\) and its relationship with heating rate, to provide a preliminary assessment of the effect of thermal lag on TMA measurements, and to investigate whether the material differences found using the DMA tests were reproduced with the TMA tests. As noted previously in Section 3.2.1, these materials were stated by the supplier to be of nominally the same material composition, varying only in thickness. It was shown in Chapter 4 that for this material, purchased in five different thicknesses, the T\(_g\) values could be separated into two distinct temperature regions, however the relationship between the heating rate dependence and thickness was
found to be independent of the material $T_g$. To investigate what impact the thickness and heating rate dependence has on the $T_g$ as measured by TMA, specimens of the System A material, 10 mm x 10 mm (of various thicknesses) were heated from 30°C to 150°C, at heating rates of 3, 5 and 10 K/min, following the same heating profile used in the DMA tests of this material shown in Chapter 4. The graphs of dimension change against temperature for specimens of 1 mm, 2 mm and 3.5 mm thickness tested at three heating rates are shown in Figures 5.1, 5.2 and 5.3 (a–c), respectively, using a new specimen for each test (specimen thicknesses of 0.25 mm and 0.5 mm are shown later). These data were analysed using the method described in Section 0 to find the $T_g$ for each test, which is plotted in Figure 5.6 and discussed later in this section.

Figure 5.4 (a) and (b) show the plot of the measured dimension change with increasing temperature for the 0.25 mm and 0.5 mm specimens tested at 10 K/min. In comparison with the results for the 1, 2 and 3.5 mm specimens, both graphs display significant noise and a sharp decrease in the specimen dimensions near the $T_g$ before returning to a steady rise (where the $T_g$ is assumed here to be in the region of 70-85°C from the values shown in the DMA tests in Section 4.3). The test was repeated on the 0.5 mm thick specimens at a further two heating rates of 3 K/min and 5 K/min and the results are shown in Figures 5.5 (a) and (b), where similar responses were observed, therefore testing was not continued at the remaining two heating rates (3 and 5 K/min) for the 0.25 mm thick material. This sharp drop in dimensions near the $T_g$ is only seen in the specimens of 0.25 and 0.5 mm thickness. Earnest (70) describes this deviation as attributable to stress relief or “alteration of the specimen morphology” and advises that if a sudden deflection such as this occurs, the test should be stopped 20°C above the temperature at which the drop takes place and the test should be started again, once the specimen has cooled. This is reflected in test standard ASTM E1545, which is based on the work of Earnest (70). ASTM E1545 suggests that difficulties may be encountered when testing specimens thinner than 0.2 mm due to difficulties in handling and it is specified in test standard ISO 11359-2 (78) that such thicknesses should be tested in the tension mode when using the TMA, so it is possible that testing in expansion mode was not suitable for thicknesses of CFRP of 0.25 and 0.5 mm.
Figure 5.1 - TMA graphs of 1 mm System A CFRP measured at (a) 3 K/min, (b) 5 K/min and (c) 10 K/min
Figure 5.2 - TMA graphs of 2 mm System A CFRP measured at (a) 3 K/min, (b) 5 K/min and (c) 10 K/min
Figure 5.3: TMA graphs of 3.5 mm System A CFRP measured at (a) 3 K/min, (b) 5 K/min and (c) 10 K/min
Figure 5.4: CFRP specimens tested at 10 K/min using TMA, of thickness (a) 0.25 mm and (b) 0.5 mm
Figure 5.5: 0.5 mm CFRP specimens tested at a) 3 and b) 5 K/min using TMA
Figure 5.6 shows the $T_g$ values measured for the 1, 2 and 3.5 mm specimens plotted against the heating rates used. Each test was repeated 3 times with a fresh specimen and all of the data points are shown on the graph. The gradients and $T_g(0)$ values from this graph have been listed in Table 5.1 for clarity. These data show that there is only a slight increase in gradient with specimen thickness. In contrast, the DMA data for the same materials (presented in Section 4.3) showed a significant increase in heating rate dependence with specimen thickness which was attributed to a greater degree of thermal lag being shown in thicker specimens. The $T_g$ values can be separated into two different regions, as seen previously for the aforementioned DMA data, in which the $T_g$ values of the 1 mm and 2 mm thick specimens were higher than that of the 3.5 mm thick specimens.

![Figure 5.6: Heating rate and thickness effects on TMA measurement of $T_g$ for System A materials.](image)

<table>
<thead>
<tr>
<th>Specimen Thickness (mm)</th>
<th>Gradient (min)</th>
<th>$T_g(0)$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>97</td>
</tr>
<tr>
<td>3.5</td>
<td>0.9</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 5.1: $T_g$ and heating rate dependence data for System A material measured by TMA
5.3 Improvements in data analysis for TMA

In the next stage, TMA testing was carried out on the System C materials, which included a CFRP and a GFRP of thickness $3.75 \pm 0.2$ mm, both composed of the same epoxy resin matrix. These materials were manufactured on-site from the prepreg stage, to ensure that the manufacture was well-controlled and to reduce any variables between the materials, other than the type of fibre used. As an additional benefit, the use of two different types of fibre reinforcement enabled evaluation of the effect of changing the fibre properties on $T_g$ measurement (i.e. highly anisotropic carbon fibre and essentially isotropic E-glass fibre), which is discussed alongside the results of this section.

In the tests on the System A material shown in the previous section of this chapter, heating rates of 3, 5 and 10 K/min were used, following the multiple heating rate test method for DMA testing. However, TMA is more sensitive to transitions when a lower heating rate is used, and in the standard, ISO 11359-2, it is recommended that heating rates should not be more than 5 K/min. Consequently, heating rates of 1, 3 and 5 K/min were used for the System C materials. In addition, a 20g weight was added to the weight tray of the instrument (previously, only the 0.05 N force exerted by the instrument was used) with the aim of acquiring better data. The greater downward force on the probe improves the contact between the probe and the specimen and therefore increases the instrument sensitivity to transitions (70).

The CFRP and GFRP specimens were heated from 40°C to 300°C at a heating rate of either 1, 3 or 5 K/min, using a fresh specimen for each test. The graph in Figure 5.7 shows the data for the first test in this series, a CFRP specimen heated at 5 K/min, where the dimension change with temperature is shown in blue, and the derivative of the dimension change with temperature is shown in red. If the recommendations for analysis outlined in test standard ISO 11359-2 are followed, it is not clear where the limits used to calculate the glass transition temperature are set. For convenience, the schematic diagram of the standard method for TMA analysis has been reproduced in Figure 5.8, which shows that the onset and end of the transition seen in the derivative graph can be used as the limits to identify the midpoint of the glass transition, which is the commonly derived value for the $T_g$. Comparing this ideal graph with that in Figure 5.7, four potential values of $T_g$ could
be derived from the data and these are marked on the graph. Point number 1 lies on the graph of dimension change against temperature, where the limits of the transition could be taken across the whole transition region. Without the use of the derivative, it would be easy to take the limits of the transition over the whole region, without any certainty that these are the most accurate limits to use. On closer inspection using the graph of the derivative (in red), it is shown that there are, in fact, multiple transitions, marked within their limits as points 2, 3 and 4.

![Graph of dimension change against temperature for System C CFRP measured by TMA, showing potential analysis points for identification of T_g](image)

**Figure 5.7:** Graph of dimension change against temperature for System C CFRP measured by TMA, showing potential analysis points for identification of T_g

In order to further investigate and identify the position of the glass transition temperature, the heating profile was altered so that specimens were heated to 250°C, cooled to 30°C, and heated a second time to 300°C. This method of testing is proposed in the test standard ISO 11359-2 as an alternative method to using a single heat ramp. In the test standard it is recommended that specimens be heated to a minimum of 50°C above the T_g in the first heat ramp. Figure 5.9 shows a sample
graph of the data from this test routine using the System C GFRP material, where the shape of the transition is seen changing on each ramp. This method can be used to eliminate the effects of relaxation of stresses built up during the cure process, which can overlap with the glass transition in the first heating run. During cure, the polymer undergoes volumetric changes due to expansion and contraction effects caused by thermal changes, as well as chemical shrinkage due to the formation of covalent bonds. Internal stresses are produced within the composite as a result of these changes, where there is a difference in behaviour between the polymer and fibre (47).

![Graph of TMA data analysis](image)

Figure 5.8: Schematic diagram of recommended method to analyse TMA data in ISO 11359-2

In order to investigate the results from each ramp in more detail, the graph in Figure 5.9 has been split into three graphs, showing the first heating, the cooling and the second heating, in Figure 5.10 (a), (b) and (c), respectively. The analysis region for the second heat ramp, Figure 5.10 (c), is much clearer. Using this method, more than one potential transition could be identified in the graph of the derivative of dimension change against temperature; the three identified previously (Figure 5.7), as well as one transition in each of the subsequent runs in Figure 5.10 (b) and (c).
Accordingly, a more detailed assessment was carried out into how to analyse TMA data when it is not the ideal curve such as the one seen earlier in Figure 5.8. In order to assess the best way to obtain a repeatable value for the $T_g$ within this wide transition region, these five analysis points were considered and recorded in Table 5.2 (GFRP data) and Table 5.3 (CFRP data). These tables show the midpoint of each transition region as identified in Figure 5.10 (a-c) for the three-stage thermal cycle. Each test was repeated five times at each of the three heating rates (1, 3 and 5 K/min) using a fresh specimen. The standard deviation for each analysis point has been given (in the green boxes) to indicate the repeatability of each point. For the GFRP material, “Point 4” as listed in Table 5.2 was not always visible in the data, and therefore not recorded. Tests on CFRP at 5 K/min were left until last. As is explained later in this section, during testing it had become clear that the $T_g$ was suitably identified from “Point 3” of the first heat ramp, therefore this set of specimens was only subjected to a single heat ramp, which was sufficient to obtain this value.

Figure 5.9: Graph of dimension change against temperature for System C GFRP tested at 3 K/min using TMA, showing two heat cycles
This test routine, in which the specimen is heated, cooled, and heated a final time, can be useful in some circumstances. However, as also noted in the standard, this test routine carries with it the risk of alteration of the polymer matrix due to the elevated temperature, which could affect test results and present data that is not representative of the “as received” material. For the purposes of evaluating TMA as a measurement technique for identification of the $T_g$ of polymer matrix composites, it is necessary to study the data of the first cycle. Furthermore, this test routine is not conducive to fast testing times, a requirement of industry. Consequently, taking data from the first heat ramp provides the most valuable information for comparison with measurements from other thermal analysis techniques, and the multiple transitions seen in the TMA data will have to be addressed.
Figure 5.10: Graph of dimension change against temperature for System C GFRP tested at 3 K/min using TMA, showing a) the first heat cycles, b) the cool down and c) the second heat cycle
Table 5.2: Comparison of the different transitions observed during TMA assessment of the 3.75 mm thick System C GFRP material

<table>
<thead>
<tr>
<th>Analysis Point</th>
<th>First Heat Ramp</th>
<th>Cooling</th>
<th>Second Heat Ramp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Point 2</td>
<td>Point 3</td>
<td>Point 4</td>
</tr>
<tr>
<td>1 K/min</td>
<td>199.6</td>
<td>214.3</td>
<td>225.4</td>
</tr>
<tr>
<td>Average</td>
<td>199.8 ± 0.5</td>
<td>214.8 ± 0.5</td>
<td>228 ± 2</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.8</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>3 K/min</td>
<td>202.3</td>
<td>215.8</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>201.1 ± 0.8</td>
<td>216.1 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.8</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>5 K/min</td>
<td>203.0</td>
<td>217.1</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>203.4 ± 0.7</td>
<td>217.7 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.8</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3: Comparison of the different transitions observed during TMA assessment of the 3.75 mm thick System C CFRP material

<table>
<thead>
<tr>
<th>Analysis Point</th>
<th>First Heat Ramp</th>
<th>Cooling</th>
<th>Second Heat Ramp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Point 2</td>
<td>Point 3</td>
<td></td>
</tr>
<tr>
<td>1 K/min</td>
<td>188.1</td>
<td>203.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>186.8</td>
<td>204.5</td>
<td>192.7</td>
</tr>
<tr>
<td></td>
<td>186.3</td>
<td>202.8</td>
<td>196.7</td>
</tr>
<tr>
<td></td>
<td>187.4</td>
<td>203.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>188.1</td>
<td>203.5</td>
<td>193.5</td>
</tr>
<tr>
<td>Average</td>
<td>187.4 ± 0.8</td>
<td>203.4 ± 0.7</td>
<td>194 ± 2</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.8</td>
<td>0.7</td>
<td>1.74</td>
</tr>
<tr>
<td>3 K/min</td>
<td>189.6</td>
<td>206.1</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>190.1</td>
<td>206.9</td>
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<tr>
<td></td>
<td>189.4</td>
<td>206.2</td>
<td>191.2</td>
</tr>
<tr>
<td></td>
<td>190.2</td>
<td>205.0</td>
<td>194.6</td>
</tr>
<tr>
<td></td>
<td>190.6</td>
<td>206.6</td>
<td>198.8</td>
</tr>
<tr>
<td>Average</td>
<td>190.0 ± 0.5</td>
<td>206.2 ± 0.7</td>
<td>195 ± 4</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.48</td>
<td>0.71</td>
<td>3.80</td>
</tr>
<tr>
<td>5 K/min</td>
<td>192.9</td>
<td>208.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>192.4</td>
<td>208.8</td>
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<td>190.5</td>
<td>207.4</td>
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<td></td>
<td>190.3</td>
<td>207.9</td>
<td></td>
</tr>
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<td></td>
<td>189.7</td>
<td>207.4</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>191 ± 1</td>
<td>208.1 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.38</td>
<td>0.73</td>
<td></td>
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</table>
As described in Section 0, the dimension change seen at the glass transition in a polymer or polymer matrix composite results from an increase in free volume that occurs as the polymer chains begin to move. A number of factors could cause multiple transitions; stress relaxation, existence of a polymer blend or small chain movement. From the data shown in Tables 5.2 and 5.3, analysis point 3 of the first heat ramp (the second transition seen in the derivative graph in Figure 5.7) had a standard deviation of less than one in all results for the TMA of this CFRP and GFRP. As highlighted in Figure 5.11, which shows a schematic diagram of the analysis, this analysis point (Point 3) showed the largest signal change, making it the simplest to interpret and thus minimising user error. The figure shows the dimension change plotted against temperature in green and the derivative of the dimension change against temperature in blue. The limits for analysis have been set as the onset and end of the major derivative dimension change, which are then used to find a midpoint in the transition seen in the dimension change-temperature plot. The use of the largest observed change as a way to locate the glass transition is in line with the theory that the $T_g$ as observed by TMA is a result of the onset of large chain movement in the matrix resin, causing an increase in free volume and expansion of the material.

Figure 5.11: Schematic showing the location of the limits used to identify the $T_g$ of System C materials
Using the region of the TMA data with the highest gradient to set the limits for locating the $T_g$ (i.e. the midpoint), the $T_g$ of the CFRP and GFRP materials measured at three heating rates are plotted against heating rate in Figure 5.12. In addition, the same tests were performed on specimens of neat resin, using the same epoxy as that of the CFRP and GFRP matrix, and analysed in the same way as the GFRP and CFRP. Whilst the heating rate dependences of the materials are similar, the $T_g$ of the resin, was higher by (10-20°C).

Figure 5.12: Graph of $T_g$ against heating rate for System C materials as measured by TMA

For the results shown in Figure 5.12, the moisture condition of the resin was unknown. In Figure 5.13, the same results were compared with TMA data for GFRP and CFRP specimens of the same material, which had been dried at 80°C for fourteen days following ASTM D5229. Drying the CFRP and GFRP specimens increased the $T_g(0)$ values by approximately 14°C for the CFRP and 29°C for the GFRP. The graph in Figure 5.13 shows that there is no change in heating rate dependence after the specimens were dried, however the values of $T_g$ shift to higher values, which can be attributed to the change in moisture levels, as it is well known
that moisture absorption lowers the $T_g$ through plasticisation (85). The GFRP displayed a higher $T_g$ than the CFRP after drying, and it is not clear why this has occurred.

![Graph of $T_g$ against heating rate for System C materials as measured by TMA; a comparison between specimens which had no conditioning and specimens which had been dried at 80°C](image)

**Figure 5.13:** Graph of $T_g$ against heating rate for System C materials as measured by TMA; a comparison between specimens which had no conditioning and specimens which had been dried at 80°C

### 5.4 Measurement of $T_g$ by DSC

The third technique explored was differential scanning calorimetry, which is widely used for thermal analysis of materials and particularly favoured by resin manufacturers and chemists. In order to draw comparisons with the previous two techniques investigated (DMA and TMA), and to assess the effect of thermal lag on this test method, DSC was used to measure the glass transition temperature of specimens also at three different heating rates. For this technique, higher heating rates of 5, 10 and 20 K/minute were used, owing to the fact that DSC is more
sensitive to heat flow changes at higher rates. Specimens were prepared using the methods described in Chapter 3.

The first set of tests was performed on the System A CFRP, which was tested at each of the three heating rates. Following the test standard ISO 11357-2, the glass transition temperature was identified for each test as the inflection point of the change in heat flow with temperature, as outlined in Chapter 3.

Figure 5.14 shows a graph of heat flow against temperature for a 2 mm CFRP specimen tested at a heating rate of 5 K/min from 40°C to 180°C. The inflection point at the glass transition has been calculated using the TA Universal Analysis software provided by the DSC manufacturer, which relies on limits set by the user. It was difficult to locate robust limits for the calculation of the inflection point, since moving the limits used to calculate these analysis points resulted in significant differences in $T_g$ (inflection point). Selection of the limits and the point of inflection relied heavily on user experience and knowledge of the material, which are not always available in situations where DSC is used, such as industry. This difficulty in analysis was present for all of the DSC data obtained for this material because the change in heat flow, which is used to identify the glass transition, was very small and often similar in scale to any noise in the signal.

The values of $T_g$ obtained for remainder of the System A materials, which were supplied as CFRP panels of five thicknesses (0.25 mm, 0.5 mm, 1 mm, 2 mm and 3.5 mm), are plotted against heating rate in Figure 5.15. In line with previous data collected for these materials using TMA and DMA, the values of glass transition temperature for the five different thicknesses of material divided into two distinct sets. However, the data show that, unlike the results for TMA and DMA, there is only a minor difference between the $T_g$ values obtained when the heating rate was changed, indicating a low heating rate dependence, or a thermal lag effect that can be considered to be negligible. No relationship between the heating rate dependence (gradient) and the material thickness can be seen, which is as to be expected from the sample preparation method where specimens were cut to dimensions no larger than 2 mm$^3$ to enable a good fit in the DSC crucible, resulting in a negligible thermal lag.
Figure 5.14: Graph of heat flow against temperature for 2 mm thick System A CFRP tested at 5 K/min using DSC

Figure 5.15: Graph of inflection point ($T_g$) against heating rate for System A materials tested using DSC
Following from the previous tests, which showed that values measured by DSC do not exhibit a significant heating rate dependence, the $T_g$ of System C neat resin GFRP and CFRP materials were measured by DSC at a single heating rate of 20 K/min. This higher heating rate was selected to ensure better instrument sensitivity, as well as being recommended in the test standard, ISO 11357-2. As an improvement on the methods used to test the System A materials, for this set of tests the specimens were smoothed on one face using abrasive paper to enable better contact with the base of the crucible, and therefore the instrument thermocouple, to increase the signal sensitivity. The resulting data are shown in Figure 5.16 and Figure 5.17. From earlier DMA and TMA data taken for this material, it was known that the $T_g$ would be in the region of 200°C, however noise in the DSC data made it difficult to locate the precise limits for finding the inflection point of the transition. Using the TA Universal Analysis software, it was possible to “smooth” the graphs and identify a $T_g$. The software performs this function using a least-squares average versus the temperature. For these data, an area of 10°C was chosen, meaning that the software grouped data for every 10°C and averaged using the method of least-squares to produce a smoother curve such as the one seen in Figures 5.16 and 5.17. The solid line in Figure 5.12 provides an example of data which has been smoothed to enable easier identification of the inflection point of the glass transition. Using this method and despite some signal noise, it was possible to obtain $T_g$ values repeatable to within 1°C, where the $T_g$ was identified as the inflection point of the transition as shown in Figure 5.16 and Figure 5.17. The full results are given in Table 5.4.

<table>
<thead>
<tr>
<th>$T_g$ (°C)</th>
<th>CFRP</th>
<th>GFRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>191.8</td>
<td>191.7</td>
<td>194.8</td>
</tr>
<tr>
<td>191.7</td>
<td></td>
<td>193.9</td>
</tr>
</tbody>
</table>
Figure 5.16: Graph of heat flow against temperature for System C CFRP measured by DSC showing smoothed (solid line) and raw data (dashed line).

Figure 5.17: Graph of heat flow against temperature for System C GFRP measured by DSC showing the smoothed (solid line) and raw (dashed line) data.
5.5 Concluding remarks

The glass transition temperature of specimens of multiple thicknesses was measured by TMA in expansion mode. For specimens of 0.25 mm and 0.5 mm thickness it was shown that this method was unsuitable, and it has been suggested that testing in tension would provide better results. CFRP and GFRP specimens were tested at multiple heating rates and it was shown that the measured $T_g$ is dependent on the heating rate used in the test, where higher values were seen at faster rates. Analysis of TMA data was shown to be more complex than the suggested guidance in test standard ISO 11359-2 for the measurement of $T_g$ by TMA.

The effect of changing the reinforcement material on the $T_g$ and heating rate dependence was studied by TMA using GFRP, CFRP and neat resin based on the same epoxy resin. It was found that the heating rate dependence differed for each material and that moisture condition must be taken into consideration when measuring the $T_g$ for comparison.

DSC was used to measure the $T_g$ of CFRP and it was shown that the low signal sensitivity caused ambiguity in the analysis of data that could lead to reduced precision. It was also shown that there is a negligible heating rate dependence for the measurement of the $T_g$ of CFRP specimens by DSC.

Due to complexity in analysis of both TMA and DSC data, it was found to be useful to use knowledge of the expected $T_g$ values from the DMA data obtained in Chapter 4 as a method of verifying the location of the glass transition. In the next chapter, a comparison is made between the three tests methods already assessed; DMA, TMA and DSC.
6  Comparison of DMA, TMA and DSC

6.1 Introduction

The glass transition temperature of a selection of polymer matrix composites has been measured using three common analysis techniques; dynamic mechanical analysis, thermomechanical analysis and differential scanning calorimetry, and the results have been presented in Chapters 4 and 5. It has been shown that the precision of these techniques can be influenced by the complexity of the data analysis, as well as thermal lag and instrument sensitivity to the glass transition. These three techniques can be used in a complementary fashion, to provide certainty over analysis points when there are multiple transitions or the transition is not clear. In this chapter, the results obtained from each technique are compared and contrasted.

6.2 Comparison of the techniques

The graphs in Figure 6.1, Figure 6.2 and Figure 6.3 show a sample of the data obtained for the measurement of $T_g$ of the system C GFRP using DMA, TMA and DSC, at heating rates of 10 K/min, 3 K/min and 20 K/min, respectively. These are the heating rates recommended for each instrument in their respective ISO standards. In the first graph, Figure 6.1, the storage modulus, loss modulus and tan delta are plotted against temperature. Figure 6.2 shows the change in dimensions with increasing temperature. Figure 6.3 is a graph of the heat flow plotted against temperature. In a side-by-side comparison, it is clear that at the glass transition, a change in signal is seen in the DMA data that is several orders of magnitude, where the presence of clear peaks for the loss modulus and tan delta and an easily identifiable inflection point in the storage modulus leave little room for variation between users. On the other hand, there is less clarity around the analysis points for both the TMA and DSC because of the impact of overlapping stress relaxations (TMA) and a poor signal to noise ratio (DSC). The smallest changes around $T_g$ can be seen in the DSC data. Therefore, the $T_g$ is most easily defined by DMA testing.
Figure 6.1 - Sample graph showing data output for DMA using System C GFRP

Figure 6.2 - Sample graph showing data output for TMA using System C GFRP
Figure 6.3 - Sample graphs showing data output for DSC using System C GFRP

Figure 6.4 (a) - Comparison of temperature-heating rate graphs for TMA, DMA and DSC of System A CFRP material at a thicknesses of 1 mm
Figure 6.4: Comparison of temperature-heating rate graphs for TMA, DMA and DSC of System A CFRP material at thicknesses of (a) 1 mm, (b) 2 mm and (c) 3.5 mm
Figures 6.4 (a-c) and 6.5 show the values for $T_g$ against heating rate as measured by DMA, TMA and DSC, plotted on one graph for two of the composite systems used; system A, and system C. $T_g$ values measured by DMA were higher by 16-23°C than those measured by TMA and DSC in all cases, even after the effects of thermal lag had been accounted for, at $T_g(0)$. Differences in glass transition temperature seen between the three techniques must therefore be attributed to the fact that they each measure a different physical property of the material: DMA measures mechanical changes, TMA measures changes in free volume due to chain movement and DSC measures calorimetric changes (55, 83, 87), where these changes begin or are measurable at different temperatures. This indicates that the DSC and TMA are more sensitive to the onset of chain mobility at the glass transition than DMA.

Figure 6.5: Comparison of temperature-heating rate graphs for TMA, DMA and DSC of System C CFRP and GFRP material
It has been shown that once thermal lag is accounted for, there are still differences in the $T_g$ values measured, therefore the next step is to consider which technique would provide the most precise data. Of the three measurement techniques investigated, then, DMA offers the greatest signal sensitivity to the glass transition, minimising variation between user analyses since there is less room for interpretation.

TMA has been popular for a few decades and, with its smaller specimen sizes, it shows a lower heating rate dependence than DMA. It was shown in this work that analysis of TMA data for polymer matrix composites can be complex, relying on user interpretation of the results. On the other hand, measurements obtained by DMA show a much higher dependence on the heating rate used, due to the thermal lag effect, than measurements by DSC and TMA, owing to the increased relative specimen size, as seen in Figure 6.6. However, using the multiple heating rate method, the $T_g(0)$ value can be identified and used to account for thermal lag effects.

Although DSC is a powerful technique, it faces limitations when used to measure the glass transition temperature of filled materials with a high volume fraction of filler (like engineering composite materials), where measurement of the $T_g$ is far less straightforward than TMA and DMA due to the low volume fraction of resin, resulting in poor sensitivity to the glass transition. DSC measurements of such reinforced materials are, in addition, greatly affected by specimen preparation, where good contact must be made between the specimen and the crucible, which sit above the thermocouple. In addition, specimen preparation is difficult for this technique, obtaining consistent size and mass of resin in particular presents challenges. As
DSC specimens are smaller in size (in the range 5-25 mg), shown in Figure 6.6 for reference, and remain in closer contact with the thermocouple than the specimens used in the other two techniques, results are less affected by thermal lag, as would be expected. In addition to these factors, faster heating rates and the opportunity to study the exotherm (which signals the degree of cure) make DSC useful; however analysis of the data can be very user-dependent due to the low signal sensitivity, and noise can easily mask the glass transition. The limitations of DSC were also noted by O’Neal et al. (87), who suggested that TMA in flexure would be the preferred technique of measuring T_g. The advances in DMA testing produced using the new method of testing at a range of heating rates (i.e. compensating for thermal lag) enable the greater sensitivity and easier analysis of DMA to be utilized. To summarise, the strengths and weaknesses of each of these thermal analysis techniques has been listed in Table 6.1.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMA</td>
<td>Very sensitive to the T_g</td>
<td>Affected by thermal lag</td>
</tr>
<tr>
<td></td>
<td>Data easy to interpret</td>
<td></td>
</tr>
<tr>
<td>TMA</td>
<td>Low heating rate dependence</td>
<td>Slow heating rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Data complex to analyse</td>
</tr>
<tr>
<td>DSC</td>
<td>Fast</td>
<td>Poor sensitivity to the T_g</td>
</tr>
<tr>
<td></td>
<td>No thermal lag</td>
<td>Data difficult to interpret</td>
</tr>
</tbody>
</table>

6.3 Concluding Remarks

A comparison between DMA, TMA and DSC was presented and it was concluded that sensitivity to the glass transition is highest in the DMA, and a correction procedure is available for the thermal lag effect which is usually considered a drawback of this technique. The other techniques are either less sensitive (DSC) or more difficult to analyse (TMA). Despite application of this correction procedure, T_g values measured by DMA, TMA and DSC still differed by as much as 22°C, indicating that the nature of the property changes being measured still have a strong influence on the T_g data.
7 Measuring the degree of cure

7.1 Introduction

In the introduction chapter and literature survey, the importance of characterising the degree of cure of polymer matrix composites was highlighted and it was shown that the $T_g$ can be a useful measure of the degree of cure. In the previous three chapters, improved methods for the measurement of the glass transition temperature using DMA, TMA and DSC were discussed and compared. This chapter presents a study of how differences in degree of cure of polymer matrix composites can be observed through the measurement of $T_g$ using each of these techniques. In addition to these three techniques, a preliminary study has been carried out into the use of FTIR as a tool for measuring the degree of cure.

The GFRP and CFRP materials characterised in this chapter were cured at different temperatures to achieve different states of cure. The degree of cure of these materials was first measured by DSC and the results are presented in the next section.

7.2 Degree of cure measurements by DSC

Differential scanning calorimetry is the technique most often used for offline characterisation of the degree of cure of composite materials (88, 89). In order to calculate the degree of cure of a composite, a sample of the uncured material is heated through its cure temperature in the DSC, and the area under the exothermic peak is quantified. This value is known as the total heat of reaction, $H_T$. Reproduced from Section 3.3.3 for convenience, the schematic in Figure 7.1 demonstrates the data analysis method. Once the total heat of reaction is obtained, the test is repeated with a specimen of the composite material for which the degree of cure is being assessed. The area under the exothermic peak for this specimen is known as the heat of reaction, $H_S$, and the ratio of this value and the total heat of reaction are used to calculate the degree of cure as follows:
\[
Degree \ of \ cure \ (\%) = \left(1 - \frac{H_s}{H_T}\right) \times 100
\quad (7.1)
\]

This method for calculating the degree of cure was applied to specimens of the System B and System C composite materials. The System B materials consisted of a range of unidirectional CFRP panels cured to four different temperatures; 150°C, 160°C, 170°C and 180°C. In order to calculate the degree of cure of the System B materials, firstly the total heat of reaction was found for the uncured prepreg of the same material. Three specimens of System B uncured prepreg were heated from 40°C to 300°C at a heating rate of 5 K/min following test standard ISO 14322 (80). The results are given in Figure 7.2 (a-c), which show the heat flow plotted against temperature for each specimen. The area under the exotherm seen between 150°C to 260°C in each graph was calculated using the TA Universal Analysis software and found to be 147.3 J/g, 149.6 J/g and 147.3 J/g for the three specimens presented in Figure 7.2 (a), (b) and (c), respectively, showing good repeatability between the three tests. An average of these three values, 148.1 J/g, was taken to be the total heat of reaction.

![Figure 7.1 - Schematic diagram for DSC data showing the area under the exothermic peak which gives the heat of reaction, H, used to calculate the degree of cure](image)

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Figure 7.2 - DSC measurements of System B CFRP prepreg tested at 5 K/min for the measurement of the total heat of reaction as part of degree of cure calculations
Following the measurement of the total heat of reaction for the System B prepreg material, specimens from the materials cured to each of the four temperatures were tested in the DSC at a heating rate of 5 K/min from 40°C to 300°C and the heat of reaction was found for each material. Using equation (7.1), the degree of cure of each material was calculated. The results are plotted in Table 7.1.

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>Degree of cure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>76</td>
</tr>
<tr>
<td>160</td>
<td>83</td>
</tr>
<tr>
<td>170</td>
<td>90</td>
</tr>
<tr>
<td>180</td>
<td>98</td>
</tr>
</tbody>
</table>

The System C materials consisted of GFRP and CFRP composed of the same matrix resin, both initially received as prepreg. In order to obtain panels at different stages of cure, an initial DSC test was performed on the prepreg material to determine a suitable cure temperature that would result in a 70% degree of cure; this would provide the flexibility to then postcure the panels to various degrees of cure without the need for multiple autoclave runs. It was previously agreed with the prepreg manufacturer that this DSC test would allow an appropriate autoclave cure temperature to be determined.

In these initial DSC trials, samples of System C GFRP and CFRP prepreg were heated in the DSC following the manufacturer recommended cure profile for this material (described in Section 3.2.3), replacing the recommended dwell temperature of 180°C with a cure temperature of either 145°C, 150°C or 160°C. After being held at one of these cure temperatures, the specimens were cooled at a rate of 2 K/min to 30°C before being taken through a final heat ramp at 5 K/min to 300°C, in order to measure the heat of reaction, \( H_s \), which was obtained from the area under the exothermic peak. The DSC data for these GFRP and CFRP test specimens are given in Figure 7.3 (a-f), where the three stages of the heat profile used in the test, as well as the analysis of the heat of reaction, are shown. In the first stage, the curing stage, the specimens were heated to an initial dwell temperature of 110°C and held for one hour before being heated to the cure
temperature indicated on each graph. In the second stage marked in each of the figures, specimens were cooled to 30°C prior to the third stage, in which specimens were heated to 300°C to measure the heat of reaction, $H_s$, which is the area under the exotherm shaded in grey.

Figure 7.3 (a) – DSC data for the System C GFRP specimen cured at 145°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_s$

Figure 7.3 (b) - DSC data for the System C GFRP specimen cured at 150°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_s$
Figure 7.3 (c) - DSC data for the System C GFRP specimen cured at 160°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_S$

Figure 7.3 (d) - DSC data for the System C CFRP specimen cured at 145°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_S$
Figure 7.3 (e) - DSC data for the System C CFRP specimen cured at 150°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_S$.

Figure 7.3 (f) - DSC data for the System C CFRP specimen cured at 160°C in the DSC which was then cooled and subjected to a second heat ramp for measurement of the heat of reaction, $H_S$. 

$H_S = 51.51$ J/g  

$H_S = 43.06$ J/g
In order to calculate the degree of cure obtained during each of the tests shown in Figure 7.3 (a-f), fresh samples of uncured GFRP and CFRP prepreg material were heated in the DSC at 5 K/min to 300°C to obtain the total heat of reaction, \( H_r \), and the degree of cure was calculated using Equation (7.1). The results are given in Table 7.2, which shows that a cure temperature of 145°C provided the desired 70% degree of cure for CFRP and gave a 74% degree of cure for GFRP.

<table>
<thead>
<tr>
<th>Cure Temperature (DSC)</th>
<th>Degree of Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GFRP</td>
</tr>
<tr>
<td>145°C</td>
<td>74%</td>
</tr>
<tr>
<td>150°C</td>
<td>77%</td>
</tr>
<tr>
<td>160°C</td>
<td>81%</td>
</tr>
</tbody>
</table>

Following the DSC trials, panels of CFRP and GFRP were cured in an autoclave following the cure profile recommended by the manufacturer, whilst limiting the final dwell temperature to 145°C as opposed to the 180°C recommended for full cure. Further details of the manufacture are given in Section 3.2.3. The degree of cure of these partly-cured panels was measured by DSC, which yielded the results given in Table 7.3. The results show that the degree of cure of the panels cured in the autoclave at 145°C reached 87% for the GFRP and 90% for the CFRP, nearly 20% higher than was predicted by the preliminary trial in which specimens were cured in the DSC. In a study of cure kinetics, Hsiao et al. (90) discussed that the total heat of reaction may vary according to the cure environment, which could explain the difference in degree of cure of the panels, cured in an autoclave, to the DSC specimens of the same material when both were subjected to the same cure profile. Separate panels were postcured at either 155°C, 165°C, 175°C or 185°C to produce specimens with different cure states. The resulting degree of cure of each panel was then measured by DSC and the results are listed in Table 7.3. The cure state of the material cured in the autoclave at 145°C has also been included. The System B and postcured System C materials were used to assess other methods of detecting degree of cure in the next sections of this chapter.
Table 7.3 – The degree of cure of System C materials cured in the autoclave at 145°C and postcured in an oven at different temperatures

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>Degree of Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GFRP</td>
</tr>
<tr>
<td>145</td>
<td>87%</td>
</tr>
<tr>
<td>155</td>
<td>93%</td>
</tr>
<tr>
<td>165</td>
<td>94%</td>
</tr>
<tr>
<td>175</td>
<td>95%</td>
</tr>
<tr>
<td>185</td>
<td>98%</td>
</tr>
</tbody>
</table>

7.3 Degree of cure by $T_g$ measurement

7.3.1 Introduction

As noted earlier, the glass transition temperature is used as an indicator of the state of cure of a composite material. In this section, the System B and System C materials, which were intentionally manufactured to varying stages of cure, have been used to assess changes in $T_g$ with degree of cure. These measurements were carried out using DMA, TMA and DSC, with regard to the effects of thermal lag in particular, and the results for each test method have been compared. In these tests, the new method using multiple heating rates (introduced in Chapters 4 and 5) has been used.

7.3.2 DMA

The System B CFRP specimens with four different degrees of cure were subjected to a heat ramp in the DMA using a heating rate of either 3, 5 or 10 K/min and heated to 280°C, using a fresh specimen for each test. The results are shown in Figure 7.4, where the $T_g$ (taken from the inflection point of the storage modulus, as described in Chapter 4) has been plotted against heating rate and the values extrapolated to find the $T_{g(0)}$. The heating rate dependence (which is the gradient of the fit line) for each of the different states of cure is very similar, showing that the thermal lag effect
is dependent on the specimen thermophysical properties, and not on the \( T_g \). This is in line with evidence shown in Section 4.3 in DMA measurements of the System A materials, where it was found that the heating rate dependence was independent of differences in \( T_g \). The individual \( T_g(0) \) values and degree of cure of each material are given in Table 7.4. The results show an increase in \( T_g(0) \) with degree of cure, as was expected. As the degree of cure progressed with each material, in stages of 7-8%, the increase in \( T_g(0) \) was reduced.

In order to validate these findings and quantify the relationship between \( T_g \) and degree of cure, the test was repeated using the System C material which had been cured at different temperatures; the cure temperature and degree of cure are shown in Table 7.5. Figure 7.5 a) and b) show the graph of \( T_g \) against heating rate for the System C CFRP and GFRP, respectively. The \( T_g \) of these specimens was measured at three heating rates of 3, 5 and 10°C, as before. As was seen in the results for the System B material (given in Figure 7.4), the heating rate dependence, which is the slope of the graph, is consistent regardless of degree of cure, while the \( T_g \) demonstrates a consistent increase with degree of cure. The degree of cure for this group of materials was between 92-100%, with only small changes of 1-3% between each cure step when compared with the results for the System B material given in Table 7.4. Between each rise in degree of cure, an increase in \( T_g(0) \) of 8-9°C was seen in the CFRP and 10-11°C was seen in the GFRP materials, meaning that for a relatively small increase in % degree of cure, there is a significant rise in \( T_g(0) \) for these materials.

Table 7.4 – The degree of cure compared against \( T_g \) of each of the System B materials cured at different temperatures

<table>
<thead>
<tr>
<th>Cure Temperature</th>
<th>Degree of Cure</th>
<th>( T_g(0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>76%</td>
<td>152°C</td>
</tr>
<tr>
<td>160</td>
<td>83%</td>
<td>169°C</td>
</tr>
<tr>
<td>170</td>
<td>90%</td>
<td>183°C</td>
</tr>
<tr>
<td>180</td>
<td>98%</td>
<td>192°C</td>
</tr>
</tbody>
</table>
Figure 7.4 – Graph of the $T_g$ against heating rate for the System B material measured by DMA

Table 7.5 – The $T_g(0)$ for System C CFRP and GFRP cured at different temperatures to four different degrees of cure

<table>
<thead>
<tr>
<th>Material</th>
<th>Cure Temperature</th>
<th>Degree of Cure</th>
<th>$T_g(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFRP</td>
<td>155</td>
<td>92%</td>
<td>183°C</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>95%</td>
<td>191°C</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>97%</td>
<td>200°C</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>~100%</td>
<td>208°C</td>
</tr>
<tr>
<td>GFRP</td>
<td>155</td>
<td>93%</td>
<td>188°C</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>94%</td>
<td>199°C</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>95%</td>
<td>209°C</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>98%</td>
<td>219°C</td>
</tr>
</tbody>
</table>
Figure 7.5 – The $T_g$ against heating rate for (a) System C CFRP and (b) System C GFRP measured by DMA

7.3.3 TMA and DSC

In the previous section the relationship between $T_g$ and degree of cure for CFRP and GFRP materials was studied. The next step, covered in this section, was to study whether the relationship between $T_g$, heating rate and degree of cure would
be reproduced using TMA and DSC as alternative and well-used methods of measuring the $T_g$. The $T_g$ measurements by TMA and by DSC are plotted against heating rate in Figure 7.6 and Figure 7.7, respectively, for Series B material specimens. The heating rate dependence appears to be negligible in the results for both the TMA and DSC tests on the specimens at each state of the cure (with the exception of the DSC result for the 170°C cure). When compared to the heating rate dependence of DMA data, this suggests, again, that both TMA and DSC are less sensitive to the effects of thermal lag, possibly because of the smaller specimen sizes used in these techniques when compared to those used in DMA testing. The data for both of the measurement techniques (shown in Figure 7.6 and Figure 7.7), show that the $T_{g(0)}$ value increased, as expected, with the degree of cure, which reflects the DMA data previously obtained.

![figure](image.png)

*Figure 7.6 – $T_g$ against heating rate for TMA measurements of System B CFRP*
7.3.4 Comparison of DMA, TMA and DSC

The results of the studies of the relationship between degree of cure and $T_g(0)$ from the three techniques (DMA, TMA and DSC), which were presented in Sections 7.3.3 and 7.3.2, have been plotted on the graph in Figure 7.8, with the results presented in Table 7.6. In the figure it is shown that, while the measured $T_g$ values vary between the techniques, the rise in $T_g$ with degree of cure follows a similar trend. It is probable that the difference between the values of $T_g(0)$ for the three techniques is due to fundamental differences in the property changes measured (e.g. calorimetric versus dynamic mechanical), as discussed in Chapter 6.

Table 7.6 – Comparison of $T_g$ measurements by DMA, TMA and DSC for System B materials with different degrees of cure

<table>
<thead>
<tr>
<th>Cure Temperature (°C)</th>
<th>Degree of Cure (%)</th>
<th>$T_g(0)$ (°C)</th>
<th>DMA</th>
<th>TMA</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>76</td>
<td>148</td>
<td>139</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>83</td>
<td>164</td>
<td>156</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>90</td>
<td>181</td>
<td>178</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>98</td>
<td>191</td>
<td>187</td>
<td>173</td>
<td></td>
</tr>
</tbody>
</table>
7.4 A preliminary assessment of FTIR as a possible method for measuring the degree of cure

7.4.1 Introduction

DSC remains one of the most popular techniques for measurement of the degree of cure of polymer composites. In addition, it was shown in the literature review in Section 2.3 that a number of other cure measurement techniques are currently being developed. This section introduces the potential for the use of Fourier-transform infrared spectroscopy (FTIR) as an alternative means for the measurement of degree of cure, with a discussion on some of the drawbacks of DSC. This is in light of a new test standard, ISO 20368, which was published during the timeframe of this project.

7.4.2 Limitations of DSC as a means of measuring degree of cure

In Chapter 5, DSC was used to measure the $T_g$ of polymer matrix composites and its limitations as a $T_g$ measurement technique were discussed in relation to the fact that the large portion of the specimen consists of “inert” material (i.e. the fibres), resulting in a low signal sensitivity to the “active” portion, the matrix resin.
Measurement of the T_g relies on identifying the temperature at which there is a change in signal. In addition, measurement of the degree of cure of a polymer matrix composite by DSC is also reliant on the measurement of the heat flow. The value of the heat flow, dH/dt, is dependent on the total mass of the composite specimen, which is input into the instrument settings prior to starting the test. The heat flow, which is the measurement output, is then calculated using the following equation (91):

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T,t)$$

Where dH/dt is the heat flow signal, C_p is the sample heat capacity, dT/dt is the heating rate and f(T,t) is the heat flow as a function of time at an absolute temperature. This mass does not take account of the “inert” fibre volume fraction, which could vary between specimens of the same material owing to the small sample sizes (approximately 3 mm^3), therefore introducing an error into the measurement of the heat of reaction when comparing samples of the same material. In an ideal scenario, it would be possible to use the fibre volume fraction to compensate for this issue, where the heat of reaction could be multiplied by the percentage resin content, or (1-V_f), however the measurement techniques available for V_f and information available on fibre density are not sufficiently accurate to be useful here. The fibre volume fraction calculations are dependent upon values of fibre density given by the material supplier, where small variations can impact the final V_f value.

7.5 FTIR measurement of degree of cure

As a preliminary assessment, Fourier transform infrared spectroscopy (FTIR) was carried out on two of the System B materials, cured at the highest and lowest temperatures (180°C and 150°C respectively) as part of the routine measurement services at the National Physical Laboratory. The resulting data are plotted in Figure 7.9, where the absorbance has been plotted against wavelength. The pink line corresponds to the material cured at 150°C (with a degree of cure of 76% as
measured by DSC) and the red line corresponds to the material cured at 180°C (with a degree of cure of 98% as measured by DSC). Highlighted in pink and green, respectively, carbonyl and aliphatic signals showed a clear difference in peak height which could be used in future to identify differences in degree of cure. This preliminary trial showed that it is possible to identify the chemical differences with degree of cure between specimens cured to 76% and 98% degree of cure.

Figure 7.9 - FTIR spectra of System B CFRP after 150°C and 180°C cure

7.6 Conclusions

The relationship between $T_g$ and degree of cure of polymer matrix composites was assessed using DMA, TMA and DSC. It was shown that despite differences in $T_g$ values between each of the three test techniques, a similar rise in $T_g$ with degree of cure was found. Application of the multiple heating rate method showed that the heating rate dependence was not affected by the degree of cure.

A preliminary study into the use of FTIR for cure assessment of polymer matrix composites was carried out and it was shown that measurable differences could be identified in the peak height relating to chemical properties that change as a consequence of the epoxy cure process, although this test was only carried out for specimens with a large difference in cure (76% and 98%).
8 Conclusions and recommendations for further work

8.1 Conclusions

The aim of this work was to improve upon the methods used for the thermal analysis measurement of \( T_g \) by addressing the parameters which impact the degree of thermal lag and, as a consequence, measurement precision.

A systematic study was carried out into the impact of heating rate, specimen thickness, fibre type (i.e. GFRP vs CFRP) and moisture condition on DMA measurement of \( T_g \) using the multiple heating rate method outlined in ISO 6721-11. Tests carried out on specimens of different thicknesses ranging from 0.25 mm to 3.5 mm showed that, regardless of differences in \( T_g \), a relationship was found between the specimen thickness and heating rate dependence attributed to thermal lag. CoDA software was used to model the diffusion of heat through DMA specimens and a new relationship was developed relating the heating rate used in DMA tests to the specimen thickness, allowing a comparable \( T_g \) to be measured for specimens of different thickness, despite the effects of thermal lag.

It was shown using the multiple heating rate test method that, despite small differences in heating rate dependence, the \( T_{g(0)} \) was not affected by changing the type of fibres for the same resin system. For the same materials it was shown that drying of specimens prior to testing increased the \( T_g \) by as much as 7°C; however, this did not affect the relationship with heating rate.

The complexities of analysis of TMA and DSC data were highlighted, where user interpretation of data could vary significantly and result in a lack of data precision. It was found that TMA measurements showed a lower dependence on heating rate than DMA, while DSC measurements were not affected.

A comparison of DMA, TMA and DSC data showed that when the effect of thermal lag is accounted for, the measured \( T_g \) values still do not agree. Due to its higher sensitivity, it was shown that DMA is the preferred method for measurement of the \( T_g \) once thermal lag is taken into account.

\( T_g \) measurements using DMA, TMA and DSC of materials at different states of cure showed that, despite differences in measured \( T_g \) values between the three
techniques, the same increase in degree of cure with $T_g$ was found. It was shown that the degree of cure did not affect the heating rate dependence of the test data.

These in-depth studies showed a number of parameters that can affect the precision of $T_g$ data and have shown the importance of reporting, fully, the test and specimen conditions. The outcome of this work will assist NPL in improving current test methods and standards.

Finally, FTIR was used to examine the degree of cure of CFRP and clear differences were seen in the peak heights for bonds that change with the cure of epoxy. FTIR has potential as a useful means of assessing cure in composite materials, which is supported by a new test standard for the use of FTIR as a means of determining the degree of cure of epoxy resins which is currently under review.

### 8.2 Recommendations for further Work

The work presented in this thesis showed that when thermal lag is accounted for, there remains a difference between $T_g$ data obtained by DMA, TMA and DSC. It would be useful as a next step to further study this difference and develop a method for relating $T_g$ measurements obtained by these three different thermal analysis techniques.

A relationship has been suggested relating heating rate to specimen thickness for comparing materials which are expected to have the same $T_g(0)$. The relationship was validated for three thicknesses for a CFRP material. It would be valuable to demonstrate that the relationship is valid on a wider range of materials (e.g. glass fibre and aramid fibre composites and thermoplastic matrices), for a range of reinforcement architectures, and a range of thicknesses.

The potential of using FTIR for use as a means of assessing the cure of polymer matrix composites was investigated briefly in this work. It was shown that this is a useful test for measurement of the degree of cure of composite materials, although additional validation is required.
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Appendix: Published Work
Heating rate effects on thermal analysis measurement of $T_g$ in composite materials

Ana X. H. Yong, Graham D. Sims, Samuel J. P. Gnaniha, Stephen L. Ogin and Paul A. Smith

Abstract Three measurement techniques used to measure the glass transition temperature ($T_g$) have been subjected to a critical comparison: dynamic mechanical analysis (DMA), thermomechanical analysis, and differential scanning calorimetry. A new procedure, whereby different specimens are tested over a range of heating rates, has been used in order to eliminate the effects of thermal lag and determine a $T_g$ independent of heating rate ($T_{g0}$). It has been shown that for measurements of $T_{g0}$ for composites, the DMA thermal lag "corrected" method gave the most reliable data. The work has provided additional guidance on these techniques that could usefully be incorporated in future standards, to improve precision, comparability, and consistency of $T_g$ measurement.

Keywords Thermal analysis, Cure monitoring, Glass transition temperature, Polymer composites

Introduction Cure assessment is important when optimizing cure efficiency during the manufacture of composite materials.

Measurement of the glass transition temperature ($T_g$) is widely used as an indicator of the degree of cure, but present standards cover a number of techniques for its determination, which are known to yield different values for the same material. The thermal lag is one factor that can compromise measured $T_g$ values because of the temperature differential between the thermocouple which provides the temperature output beside the specimen and the temperature within the specimen. As the oven temperature is ramped continuously throughout the test, the specimen temperature lags behind.

A new test method was introduced in standard ISO 6521-117 which serves to correct for the effect of thermal lag in dynamic mechanical analysis (DMA) measurements using different specimens of the same material to measure the $T_g$ at a range of heating rates, the $T_g$ at zero heating rate (or $0^\circ$ C/min), known as the $T_{g0}$, is then found by extrapolation. In the present study, this new method has been applied to DMA, and extended to thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). The aim is to clarify how changes in applied heating rate can affect the thermal analysis and cure measurement of polymer matrix composites, as well as investigating the relationship between these three techniques commonly used in industry, and other testing aspects (e.g., specimen thickness).

Materials and measurement techniques

Materials

Three types of fiber-reinforced epoxy resin system (systems A, B, and C) were used to study the effects of specimen thickness, degree of cure, and fiber reinforcement on thermal analysis measurements.

System A material was a woven carbon fiber/epoxy composite (CFPR) purchased in five thicknesses: 0.25, 0.5, 1.2, and 1.5 mm. These materials were described by the supplier as nominally the same material varying only in supplied thickness: The material was tested in the as-received condition.

The System B material was a unidirectional carbon-fiber/epoxy, received as uncurled prepreg, which was laminated (16 plies; unidirectionally aligned) and cured at four different
temperatures. The panels were held for two hours at 150, 160, 170, and 180 °C following a 3 °C/min heating rate to produce four panels at different states of cure. The panels were 300 mm x 300 mm in area, with a cured panel thickness of 2 mm. Prior to testing, System B test specimens were dried for seven days at 80 °C and stored in a controlled environment at 23 ± 2 °C and 50 ± 5% relative humidity.

System C materials were manufactured using prepregs of the same commercial epoxy resin reinforced with either five-harness satin weave carbon-fiber cloth of fiber areal weight 285 g/m² or a four-harness satin weave glass-fiber cloth of fiber areal weight 100 g/m². All panels were cured with the autoclave cycle recommended by the manufacturer (i.e., temperature ramped at 3 °C/min to an initial hold temperature of 110 °C for one hour, subsequently raised to 180 °C at 3 °C/min and held for two hours). The majority of the specimens were stored under ambient conditions and a single set of DMA specimens were dried at 80 °C before testing. The System C group of materials also included a 30 mm x 15 mm x 3.5 mm plate of the same epoxy resin (unreinforced), which was cured for two hours at 180 °C following a ramp rate of 0.5 °C/min from ambient (23 °C) to 180 °C.

Measurement techniques

Three thermal analysis methods have been used for comparison. Firstly, DMA has been undertaken using a TA Instruments Q800 dynamic mechanical analyzer, according to ISO 6721-11. A characteristic DMA graph for CFRP, showing the common analysis points for use in identification of the $T_d$ values. Figure 1 shows a characteristic DMA output. The relationships shown in the box in Figure 1 are used to calculate the tan delta, loss (tangent) modulus, and storage (elastic) modulus, which are calculated by the instrument software from the stress and strain data, and the phase difference between them. The Q800 instrument employs an optical encoder to measure the displacement (which the instrument software converts to strain) throughout the test. The $T_d$ is often obtained from either: (1) the peak of the loss modulus; (2) the peak of the tan delta curve; or (3) the inflection point in the storage modulus curve (sometimes the onset of the drop in storage modulus is used), as indicated in Figure 1. Specimens tested were 10 mm x 25 mm (w x l) with different thicknesses in the range 0.25-4 mm. All panels were tested using a single cantilever beam configuration with fibers (unidirectional or woven) parallel to the length of the specimen. For each test, the instrument was set to equilibrate at 30 °C prior to the heating cycle. Specimens were heated at a rate of 3.5 or 10 °C/min to a final temperature of 180 °C for System A, 250 °C for System B, and 300 °C for System C. The final test temperatures for each material were selected based on the $T_d$ measurement obtained from an initial test in which a specimen was heated at a ramp rate of 10 °C/min to a final test temperature of 350 °C, or lower, if the test temperature had clearly passed through the specimen. The final temperature selected for the subsequent runs was set to at least 50 °C above the nominal $T_d$ of the material, as outlined in ISO 6721-11. A frequency of 1 Hz and oscillation amplitude of 10 °C were used, and tests were carried out in static air. The measured $T_d$ was plotted against heating rate, with results extrapolated in order to determine the $T_d$ for zero heating rate, $T_{d0}$ following the standard ISO 6721-11. In addition, the heating rate dependence for each material system was determined from the slope of the data in each case (see Figure 2).

TMA measurements were performed for System B materials using a TA Instruments Q400 thermomechanical analyzer in compression mode. During the test, the linear movement of a probe, located on the specimen, was used to measure the expansion change via an LVDT, when the expansion is plotted against temperature, the $T_d$ is identified as a point within this transition region. Following the analysis method outlined in ISO 11359-2009, the $T_{d0}$ was taken as the midpoint of the transition region, using the first derivative of the dimension change with temperature as a means of indicating the limits of the transition, as shown in Figure 3. In order to identify the $T_{d0}$, the major dimension change, and the onset and end of
this major change were identified with the aid of the derivative. Figure 4 shows an example where the end of the major dimension change is the peak in the derivative (at 214 °C in this case), and the onset is the change in slope of the derivative (at 198 °C). The $T_{m}$ was then taken to be at the midpoint of these two measurements (in this case, at 207 °C). This technique could be applied to all measurements and provided a consistent measurement of $T_{m}$. The TMA specimens (length, width, and thickness: 10 mm x 10 mm x 2 mm) were tested in the through-thickness direction using a preload force of 0.05 N, which ensures good contact between the probe and the specimen. Following equilibration at 30 °C, Series A and B specimens were heated to 150 and 250 °C, respectively, at a rate of 3, 5, or 10 °C/min. The thermal lag approach was then applied to find $T_{ps}$ for both series.

The DSC measurements of $T_{g}$ and degree of cure were made using a TA Instruments Q2000. The instrument was calibrated using an Indium temperature reference standard (NIST 2232) and a nitrogen gas at a flow rate of 50 ml/min was used in every test. In DSC, $T_{g}$ was observed as a deviation in the heat flow to the specimen as it undergoes a change in heat capacity. In order to measure the $T_{g}$, specimens were heated from 30 to 250 °C using a heating rate of 5, 10, or 20 °C/min. Higher heating rates than those employed for DMA and TMA were used, following guidance set out in ISO 11357-2:2014. The $T_{g}$ was taken as the inflection point of the heat flow curve as shown in the example plot in Figure 6, again, the thermal lag approach was adopted to find $T_{g}$. 
Following ISO 14322-2-2012, the degree of cure was measured using the exothermic peak in the DSC measurement of heat flow. The uncurled prepreg was heated at 5 °C/min to 300 °C to obtain the total heat of reaction (Figure 5). The degree of cure of the material was calculated using Equation 1.\textsuperscript{a}

\[
\text{Degree of cure (\%)} = \left(1 - \frac{H_r}{H_t}\right) \times 100
\]

where \(H_r\) is the heat of reaction of the specimen being assessed (not shown in Figure 5) and \(H_t\) is the total heat of reaction obtained from measurements performed on the uncurled prepreg.

Cured specimens were cut to approximately 2 mm × 2 mm × 2 mm to fit the TA Instruments Tzero crucibles and smoothed using wet and dry paper to optimize contact with the base of the crucible and therefore with the thermocouple. Uncured prepreg specimens were similarly cut to 2 mm × 2 mm squares. Thermal contact between prepreg layers was ensured through natural tack and local compression provided by the TA Instrument’s crucible press. The masses of polymer matrix equated to 0.3–0.4 of the total sample masses, which were in the range 2–10 mg for prepreg and 5–25 mg for the cured material, depending upon the practicalities of ensuring good contact with the crucible.

**Results and discussion**

**Thickness effects on the measurement of \(T_p\) (System A materials)**

Figure 6a–e show the measured \(T_p\) values against heating rate for each of the five thicknesses of the System A materials using the three common analyzers: point, the storage modulus, and the peak of the tan delta curve. The data show that the peak of the tan
Figure 7 Graph of the heating rate dependence on specimen thickness for DMA of Series A CFRP using (a) storage modulus inflection point; (b) loss modulus peak; and (c) tan delta peak as a measure of $T_R$. Data points with brackets [ ] are considered unreliable as the beam was too thin.

Figure 8 Graph of inflection point against heating rate for DMA of Series A CFRP showing effect of specimen thickness on $T_R$ measurement.

The delta curve gives the highest value of $T_R$ with respect to the other two analysis points; the same relative values of $T_R$ have been described in other work, though not for tests at different thicknesses. For laminate thicknesses of 1 mm and above, the storage and loss modulus (the same value of $T_R$) for thicknesses below 1 mm (i.e., at 0.25 and 0.5 mm specimen thicknesses), the quality of the data was compromised due to significant noise, indicating that the DMA test method using this flexural mode is not suitable for these specimen thicknesses. The results indicate that the inflection of the storage modulus is the best choice for analysis as it provides the least scatter and therefore the most reliable data.

Gradients of the graphs in Figure 6(a)–(c) are shown plotted against specimen thickness in Figure 7 for the three measurement points. The data show that the degree of thermal lag is dependent on specimen thickness. The smallest specimen thickness (0.25 mm) does not appear to follow the trend closely, but there is more noise in the results for the thinner specimens; DMA testing in tension, as opposed to flexure, could provide a better alternative and give more consistent data for very thin specimens. Figure 7 suggests a potential normalization of data for different thicknesses using a ‘calibration curve’ of this type.

Table 1 Comparison of $T_{on}$ values for System A materials by DMA, TMA, and DSC

<table>
<thead>
<tr>
<th>Specimen Thickness (mm)</th>
<th>DMA ($T_{on}$)</th>
<th>TMA ($T_{on}$)</th>
<th>DSC ($T_{on}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 mm</td>
<td>75.0</td>
<td>Too thin for test</td>
<td>92.3</td>
</tr>
<tr>
<td>0.5 mm</td>
<td>74.4</td>
<td>Too thin for test</td>
<td>88.0</td>
</tr>
<tr>
<td>1 mm</td>
<td>113.0</td>
<td>107.2</td>
<td>103.4</td>
</tr>
<tr>
<td>2 mm</td>
<td>121.1</td>
<td>97.1</td>
<td>106.8</td>
</tr>
<tr>
<td>3.5 mm</td>
<td>72.0</td>
<td>82.4</td>
<td>93.2</td>
</tr>
</tbody>
</table>

Further inspection of the System A materials provides information on the material and the thermal lag effect. Figure 8 shows the storage modulus inflection point data for all of the specimen thicknesses compared on one graph, indicating that the different thicknesses of material can clearly be separated, in terms of $T_{on}$, 112–115 °C for the 1 and 2 mm material, and 70–85 °C for the 0.25, 0.5, and 3.5 mm material. The observation has been independently verified by the TMA and DSC test data shown in Table 1. The difference is large enough to be a concern to end-users and product design insofar as these materials are supplied as nominally identical – albeit of different thicknesses. The observation that the results in Figure 7 fall onto one line, regardless of $T_R$, suggests that the heating
rate dependence is a consequence of the thermal lag in the test, which is dominated by the thermophysical properties of the specimen, as opposed to the $T_g$, which is a property of the matrix resin. It is likely that the thermal lag effect is dependent on the material diffusivity as DMA specimens are tested under dynamic conditions and the important physical feature in this test is the rate at which heat permeates through the material.

The difference in $T_g$ that is observed between values measured by DMA, TMA, and DSC in Table 1 can be attributed to the fact that each technique measures a different physical property, where TMA shows changes in free volume due to chain movement, DSC measures enthalpic changes and DMA measures mechanical changes. These changes could begin to be measurable at different temperatures.

Cure effects on $T_g$ measurements (System B materials)

The DMA results for the System B materials cured to four different states of cure are shown in Figure 8 and demonstrate an expected increase in $T_g$ with increased cure temperature. The heating rate dependence of the specimens at the four cure temperatures are very similar, giving further indication that the thermal lag effect is dependent on the specimen thermophysical properties, and not on the $T_g$.

The $T_g$ measured by TMA and by DSC are plotted against heating rate in Figures 10 and 11 for Series B material specimens. For both techniques, the heating rate dependence appears to be negligible for all of the cure conditions (except, perhaps, for the DSC result for the 170°C cure). This suggests that both techniques are less sensitive to the effects of thermal lag, possibly because of the smaller specimen sizes used for TMA and DSC, when compared to DMA. For all three measurement techniques, the $T_{am}$ value increases, as expected, with the degree of cure (Figure 12). It is probable that the difference between the values of $T_{am}$ for the three techniques is due to fundamental differences in the property changes measured (e.g., calorimetric versus dynamic mechanical). Of the three measurement techniques investigated, DMA offers the greatest signal sensitivity to the glass transition and the $T_{am}$ value can be identified after accounting for thermal lag.

Figure 8 Graph of storage modulus inflection point against heating rate for DMA of Series B CFRP

Figure 10 Graph showing the change in measured $T_g$ with heating rate for TMA of Series B CFRP
effects. The limitations of DSC were also noted by O’Neal et al., who suggested that TMA in fixture would be the preferred technique of measuring $T_g$. However, the advances in DMA testing produced using the new method of testing at a range of heating rates (i.e., compensating for thermal lag) enable the greater sensitivity of DMA to be utilized.
Effect of fiber reinforcement type on $T_g$ measurement (System C materials)

In these tests, System C materials (CFRP, GFRP, and neat resin specimens), manufactured using the same epoxy resin, were tested using DMA in order to evaluate the effects of fiber reinforcement type on $T_g$. These rate-dependent data were compared with DSC data which were obtained at a single heating rate, 20 °C/min, after previous work on Systems A and B showed that the effect of heating rate was negligible. Figure 14 shows that the $T_g$ values were very similar for the CFRP, GFRP, and neat resin specimens, with small heating rate differences. Timplu and coworkers [16] obtained the thermal diffusivity of CFRP to be higher than GFRP from which it would be expected that the heating rate dependence would be lower for the CFRP specimens (i.e., a nontemperature lag). However, as noted in Good Practice Guide GPG62 [18], the reference specimens made with higher thermal conductivity materials showed a higher heating rate dependence, which may be attributable to detailed material/heat/interaction. Interestingly, the same heating rate dependence was obtained for each type of specimen when dried to a constant weight (see Figure 14) as the ambient stored specimens.

Concluding remarks

The results obtained indicate that measuring the $T_g$ using the inflection point of the storage modulus measured by DMA and using the new method of testing different materials at a range of heating rates is the preferred method for identifying the $T_g$ of a polymer matrix composite. Sensitivity to the glass transition is higher in the DMA, and a correction procedure is available for the thermal lag effect. Other techniques are either too sensitive (OSC) or more difficult to analyze (TMA). The data obtained for different temperatures of nominally identical material, suggest that the heating rate dependence of the thermal lag can be normalized using a calibration curve. These studies have provided additional guidance on the application of these techniques that could be usefully incorporated into future standards, as a means to increase precision, comparability, and consistency of $T_g$ measurement.

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