Hyperbranched polymers and their silica hybrids as epoxy resin modifiers

by

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Abstract

One of the greatest limitations to the use of polymer composites is the high cost of the techniques traditionally employed in their manufacture. Therefore, less labour intensive, lower cost manufacturing methods such as resin transfer moulding (RTM) have been developed. Such processes require a resin with low viscosity at the processing temperature. Resins that exhibit good high temperature performance tend to be viscous, and are usually brittle when cured. Conventional toughening agents, such as polyethersulfone, further increase the viscosity of the blend.

This work focuses on the use of hyperbranched polymers as resin additives, as these low viscosity materials can have the potential to act as toughening agents. It was hypothesised that the thermal properties of the blend could be simultaneously enhanced by the incorporation of a thermally stable inorganic phase, and as such the synthesis of organic-inorganic hybrids was investigated.

Organic-inorganic hybrids of a commercially available hyperbranched polyester, Boltorn E1, were synthesised using two hydrolytic sol-gel methods. In both methods the inorganic phase was silica; one process was carried out in solution, the other was an emulsion method. The sol-gel processes were carried out under comparatively mild conditions and so allowed the introduction of organic material that would be degraded by high temperature processing. Both methods yielded nano-scale hybrid products, as confirmed by electron microscopy and infrared spectroscopy studies. Particulate hybrids of Boltorn E1 and silica, of approximately 100 nm diameter, were successfully synthesised using the emulsion method.

The use of hyperbranched polymers as additives to epoxy resins was investigated, both as the organic component of organic-inorganic hybrid additive, and as resin modifiers in their own right. The addition of Boltorn E1 failed to increase the fracture toughness of a variety of epoxy resins. The reasons for this were identified. The addition of hybrid particles did not enhance the thermal properties of a trifunctional epoxy resin, as the additive sterically inhibited resin cross-linking. It was hypothesised that reducing particle size and agglomeration would prevent this plasticising effect.
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<td>ACG</td>
<td>Advanced Composites Group</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>ARES</td>
<td>Advanced rheometric expansion system</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>bv</td>
<td>By volume</td>
</tr>
<tr>
<td>CTBN</td>
<td>Carboxy-terminated butadiene acrylonitrile</td>
</tr>
<tr>
<td>DB</td>
<td>Degree of branching</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabiocyclo(5.4.0)undec-7-ene</td>
</tr>
<tr>
<td>DDS</td>
<td>4,4'-Diaminodiphenylsulfone</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidylether of bisphenol A</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>G(_{1c})</td>
<td>Critical strain energy release rate</td>
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<tr>
<td>GPTMS</td>
<td>3-Glycidoxypropyltrimethoxysilane</td>
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<tr>
<td>HBP</td>
<td>Hyperbranched polymer</td>
</tr>
<tr>
<td>HEA</td>
<td>2-Hydroxyethyl acetate</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>K(_{ic})</td>
<td>Critical stress intensity factor</td>
</tr>
<tr>
<td>NHSG</td>
<td>Non-hydrolytic sol-gel</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PAMAM</td>
<td>Polyamidoamine</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PES</td>
<td>Polyethersulfone</td>
</tr>
<tr>
<td>phr</td>
<td>Parts per hundred resin by mass</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>RTM</td>
<td>Resin transfer moulding</td>
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<td>SAXS</td>
<td>Small angle X-ray scattering</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>St dev</td>
<td>Standard deviation</td>
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<tr>
<td>T(_g)</td>
<td>Glass transition temperature</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetric</td>
</tr>
<tr>
<td>TGDDM</td>
<td>Tetraglycidyl-4,4'-diaminodiphenylmethane</td>
</tr>
<tr>
<td>TGPPAP</td>
<td>Triglycidyl-p-aminophenol</td>
</tr>
<tr>
<td>TMOS</td>
<td>Tetramethoxysilane</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>VARTM</td>
<td>Vacuum assisted resin transfer moulding</td>
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<tr>
<td>WAXD</td>
<td>Wide angle X-ray diffraction</td>
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<td>XPS</td>
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Chapter 1: Introduction
1.1 Introduction

Carbon fibre reinforced polymeric composites are increasingly being considered as construction materials for various military and civil aerospace applications [1]. This can be attributed to the advantageous characteristics that they offer in comparison to more traditional structural materials, such as metals. Most prominent is the potential for weight reduction, owing to the high specific stiffness and strength characteristics that they possess, together with potential for improved fatigue behaviour. Disadvantages can be high manufacturing costs, inferior hardness and poorer high temperature capabilities compared to metals.

The factors responsible for the properties of composites are complex; the main constituents of the material, i.e. fibrous reinforcement and polymeric matrix, each exert a substantial influence on behaviour. Although the fibrous phase provides most of the strength and stiffness requirements, many key composite properties are matrix dependent. For example, the ability to withstand temperature extremes and humid atmospheres is controlled largely by the matrix phase, as are important issues such as impact behaviour and damage tolerance.

One of the greatest limitations to the use of polymer composites is the high cost of the labour intensive techniques traditionally employed in their manufacture. Autoclave cure involves the hand lay up of sheets of pre-preg, as such it involves a large number of man-hours. Therefore, less labour intensive, lower cost manufacturing methods, such as resin transfer moulding (RTM) and vacuum assisted RTM (VARTM), have been developed. In such processes the resin is pumped into a mould containing the reinforcing fibres. Hence, a resin with low viscosity at the processing temperature is required in order that the resin flows into the mould and completely wets the fibres to result in a void-free product. Such matrix resin systems are commercially available but their thermal and mechanical properties are generally inferior to those resins used in pre-preg manufacture.

Many aircraft structural applications require materials that exhibit good high temperature performance over a long lifetime, implying a high cross-link density in the case of polymeric materials. Therefore, a tetrafunctional epoxy, with the potential to exhibit a high glass transition temperature ($T_g$), has been employed for most applications. This resin system is viscous and, as such, its composites must be manufactured using pre-preg techniques. Such high-functionality epoxies exhibit a
variety of benefits in comparison to other polymers and, therefore, currently form the basis of most aerospace structural matrix resin and adhesive formulations. Despite possessing substantial elevated temperature capabilities, such highly cross-linked thermosetting polymers are usually brittle. The most successful toughening methods thus far employed involve the addition of high molecular weight thermoplastic, typically polyethersulfone (PES), to the thermosetting matrix. However, these additives dramatically increase the viscosity of the blend, impairing its processability [2].

Thus, one objective of the current programme has been to develop polymeric formulations having a low viscosity, combined with thermal and mechanical properties of sufficient magnitude to impart improved composite performance in comparison to current, commercially available, systems. This work focuses on the use of dendritic polymers as resin additives, as these globular molecules have the potential to act as both rheology modifiers and toughening agents for matrix resins [3-5]. It was hypothesised that the thermal properties of the blend could be enhanced by the simultaneous incorporation of a thermally stable inorganic phase.

The remarkable property improvements that can result from the incorporation of inorganic material into organic polymers are becoming apparent as a result of worldwide research. Incorporating inorganic species as nanometre sized dispersions, within organic systems has been shown to be particularly effective [6-10]. Improvements in properties such as high temperature performance, strength and stiffness, together with substantial reductions in flammability, moisture transmission and thermal expansion/contraction behaviour have been particularly noteworthy. Thus, one objective of this study has been to consider nano-hybrids with a view to their potential exploitation in aircraft structures.

One of the major classes of organic-inorganic hybrids comprises those derived from inorganic oxides, formed by the sol-gel process [11]. These inorganic materials are ceramics. Conventional ceramic processing involves very, high temperatures (greater than 1200 °C) [12, 13]. In contrast, the sol-gel process is carried out under comparatively mild conditions and so allows the introduction of organic material that would be degraded by high temperature processing.

Owing to the exceptional properties of hybrids, in particular when nano-scale morphology is achieved, they have potential as additives to structural polymer
resins. It is anticipated that the addition of these materials to conventional polymers, such as epoxy resin systems, could enhance both their mechanical and thermal properties. For example, the organic phase can be selected to toughen the resin whilst the inorganic component has the potential to enhance its thermal stability.

1.2 Dendrimers and hyperbranched polymers (HBPs)

1.2.1 Introduction

Non-linear polymeric structures have received much attention in recent years, owing to both the interesting topologies and unusual properties these polymers may exhibit. Non-linear polymers contain one or more branching points where polymeric chains meet. Examples of some basic polymer structures are shown in figure 1.1 [14].

![Linear polymer](image1)

![Star polymer](image2)

![Dendrimer](image3)

![Hyperbranched polymer](image4)

*Figure 1.1: Polymer structures [14]*
1.2.1.1 Historical background

In 1952 Flory [15] published theoretical work on HBPs formed by the random polycondensation of multifunctional monomers. Highly branched polymer structures had been known to exist in the form of polysaccharides since the 1930s, however the first intentional synthesis of an HBP did not take place for another fifty years [16].

The first dendrimer synthesis was attempted by Vögtle and co-workers [17] in the late 1970s. Vögtle’s synthesis involved Michael-type addition of acrylonitrile to an amine, followed by reduction of the nitrile groups to primary amines. These two steps theoretically could be repeated in an iterative manner to build up a high molecular weight polymer. However, this synthesis proved difficult and yields were low.

In 1979 work began by Tomalia at the Dow Chemical Company on the synthesis of starburst™ dendrimers [18]. These are polyamidoamine (PAMAM) dendrimers and are now available commercially [19]. The synthesis involves Michael addition of methyl acrylate to an amine core, followed by amidation of the resultant esters. The dendrimer is synthesised by the repetition of these two steps, high yields have been achieved at each step [20]. The term “dendrimer” was first coined for these materials [20]. Polymers developed by Newkome and co-workers [21-23], at around the same time, had a similar structure to these dendrimers but each layer added had a different composition. These materials were named “arborol” structures.

In the last two decades interest in dendrimers and HBPs has been great, and as such many reviews of these materials have been published [3, 24-29].

1.2.1.2 Molecular architecture

Dendrimers consist of a central multifunctional core to which arms, built up of successive generations of branching units, are bonded [8]. A new generation is produced when a series of monomers is reacted onto each of the peripheral active ends of the dendrimer. The number of groups added at each stage increases exponentially with generation number.
This structure gives the polymer a tree-like appearance, hence the names "dendrimer" [20] or "arborol" [21-23] (dendra is Greek for tree, whilst arbor means branch) for these molecules. The structure of a fourth generation dendrimer is shown in figure 1.2 [24]. C represents the dendrimer core; the functional groups in generations 1, 2 and 3 are denoted X, Y and Z; S represents a fourth generation group.

Figure 1.2: Dendrimer structure [30]

In figure 1.2 it can be seen that as generation number increases, so steric crowding at the surface of the molecule increases. The number of monomer units in a dendrimer increases exponentially with generation number, whereas the available space for subsequent generations increases with the cube of the generation radius. Therefore, there will be a point beyond which the dendrimer cannot grow due to steric constraints. This point is known as the "starburst limit" [31]. At higher generation numbers than this limit the surface groups are forced to adopt a globular conformation.

HBPs are a class of highly, but imperfectly, branched polymers related to dendrimers [3, 24, 27]. The polymers are built up by the random addition of multifunctional monomers in one step [32] to give a highly branched globular structure; they do not have a well-defined core. Little control can be exercised over the reaction so the products are polydisperse. The monomers from which HBPs are synthesised are multifunctional [26]. Branching does not occur at every monomer, therefore, linear units are present.
The globular topology of dendrimers and HBPs imparts material properties that are rather different from those of their linear analogues [33]. Linear polymers have a more open, flexible morphology and so their chains are more able to entangle. Therefore, a dendrimer or HBP will have a lower viscosity and a higher solubility than its linear analogue because of the respective degrees of chain entanglement possible. An example of the solubility effect is given by polyphenylene. Linear poly-\textit{p-}phenylene is one of the most intractable polymers known, whereas hyperbranched polyphenylenes [25, 34] and polyphenylene dendrimers [35] are soluble in various organic solvents.

1.2.2 Synthesis of dendrimers

There are two main routes to dendrimer synthesis, divergent [18] and convergent [36] growth. In the divergent growth approach monomers are added to the surface of the molecule, building outwards from the multifunctional core, to construct subsequent generations of the polymer. The convergent approach begins at what will be the periphery of the dendrimer and works inward coupling units together to form progressively larger dendrons (wedges), which are finally linked to the central core.

Dendrimer synthesis involves many steps, as generations must be built up one by one often with protection and deprotection steps involved [37]. Therefore it can be a time-consuming and laborious process, with a high yield required from each reaction. In order to achieve perfect branching, monomers with one reactive and one unreactive end must be added to the core [20, 38], so that only one layer of monomer molecule adds to the peripheral groups. The unreactive end becomes the new surface of the molecule, which may then be deprotected. The two states, with unreactive and reactive functional groups at the periphery, are known as half- and full-generation respectively.

An example of this activation process is shown in figure 1.3 [38]. The reaction of 5-nitroisophthaloyl dichloride with two equivalents of aniline yielded the nitro functionalised wedge (inactive half-generation), which was then reduced to give the amino moiety (active full-generation). A further generation may then be added by repeating the two steps.
1.2.2.1 Divergent growth

In early dendrimer syntheses divergent growth was used [15, 20-23, 39]. With each new generation added to the molecule the molar mass of the dendrimer is doubled. Isolation of the desired dendrimer product is virtually impossible, as any by-products formed will have very similar structures to the perfect dendrimer.

Figure 1.4 shows the first one and a half generations of divergent growth of a PAMAM dendrimer from an ammonia core, using the Dow synthesis [40]. The addition of methyl acrylate to ammonia to give the half-generation triester is followed by amidation by the addition of a large excess of ethylenediamine to give the first-generation compound.

![Diagram of dendrimer synthesis]

**Figure 1.4:** Two-stage process involved in PAMAM dendrimer synthesis [40]
1.2.2.2 Convergent growth

The convergent approach to polymer growth was originally proposed and developed by Fréchet and Hawker [41-44] several years after the advent of divergent synthesis. This method of growth begins at what will be the surface of the dendrimer and works inwards, coupling monomers to the incipient dendrons. Once the dendrons are of the required generation they are coupled to a multifunctional core. First, two surface units react with two functional groups on a single monomer. The monomer will have a third functional group (the ‘focal point’) that is protected or inactive during this coupling step. A second reaction then activates the focal point so the coupling process can be repeated.

Fréchet and Hawker initially worked on the convergent synthesis of polybenzylether [41, 42]. The first step of their protocol is shown in figure 1.5. The alcohol is converted to the corresponding bromide by reaction with carbon tetrabromide and triphenylphosphine. Repetition of these two steps up to the sixth generation was carried out and the dendrons attached to a trifunctional 1,1,1-tris(4'-hydroxyphenyl)ethane core.

![Convergent synthesis of a polybenzylether dendron](image)

**Figure 1.5: Convergent synthesis of a polybenzylether dendron [41]**

The convergent synthesis of dendrimers has expanded beyond polybenzylether to become a general method of dendrimer synthesis. Other systems in which it has been use include triazines [38], siloxanes [45] and ureas [46]. This method allows control of the number and position of end groups of the dendrimer [43]. Purification of convergently grown dendrimers is far simpler than for divergently grown molecules as by-products, or the products of incomplete reactions, are significantly different from the perfect dendron structure.
1.2.2.3 Alternative growth techniques

Fréchet's group worked on improving and, in particular, speeding up, dendrimer synthesis. This led to the development of hypercores [47] and branched monomers [48] for convergent synthesis. These are pre-branched versions of traditional cores and monomers, hence reducing the number of steps and margin for error in dendrimer synthesis.

Methods of dendrimer synthesis that do not require activation steps have been developed [49]. One of these approaches uses two different sorts of monomer with different functional groups, denoted AB₂ and CD₂ monomers, where A and C react with D and B respectively. If the functional groups are correctly chosen intermediate purification steps are not required. An example of such a method is the synthesis of polyetherurethane dendrimers [50] from 3,5-diisocyanatobenzyl chloride and 3,5-dihydroxybenzyl alcohol.

One-pot synthetic methods have been developed for the divergent synthesis of dendrimers. These are carried out by two sets of reaction conditions being applied alternately to the reaction mixture, i.e. an orthogonal system [51]. Excess reagent is removed by distillation at each stage. This method allows less time-consuming divergent synthesis [52].

1.2.3 Synthesis of HBPs

HBPs are prepared by a one-pot synthesis, allowing them to be prepared more quickly and easily than their dendrimer analogues; however, less control can be exerted over the reacting species. Therefore, products with a polydispersity far greater than one may be formed. Nevertheless, hyperbranched aliphatic polyesters with a polydispersity of only 1.13 have been achieved [53].

Not every functional group is able to react because of steric hindrance, so at some potential branching points only one functional group reacts to give a linear unit, or no reaction at all occurs leading to a terminal unit.
Many of the properties of HBPs are governed by their degree of branching [17] (DB), which may be defined as the fraction of monomers that are incorporated dendritically and terminally [55]. The values commonly observed for HBPs are in the range 0.4 to 0.8 [55]. The higher the DB the more closely the polymer approaches a dendrimer. A linear polymer would have DB= 0 and a perfect dendrimer DB= 1.

1.2.3.1 Polymerisation of ABₘ monomers

The synthetic procedure most commonly used in the preparation of HBPs is the one-step reaction of multifunctional monomers, known as ABₘ monomers (having one functional A group and \(m\) complementary B functional groups per molecule) in which, most often, \(m=2\). To obtain maximum branching A and B must react with each other in the absence of side reactions. The reaction of A and B may be by condensation [54, 56, 57], addition [32] or ring-opening [58] polymerisation.

Figure 1.6: Synthesis of hyperbranched polyphenylene [54]

An example of HBP synthesis by the condensation of AB₂ monomers is given in figure 1.6 [54]. This procedure, for the synthesis of hyperbranched polyphenylene, was developed by Kim at DuPont.

Hyperbranched analogues of Tomalia's PAMAM dendrimers have been synthesised [32, 59] by the addition polymerisation of aminoacrylate hydrochloride AB₂ monomers. 'A' represents a Michael acceptor (in this case the acrylamide group), and 'B₂' a primary aliphatic amine. In the subsequent melt polymerisation reaction
the amine group adds across an acrylate C=C double bond to give the hyperbranched polymer.

1.2.3.2 Alternative polymerisation routes

Alternative methods for the synthesis of HBPs have been developed [60]. One such method is self-condensing vinyl polymerisation, developed by Fréchet [61] (figure 1.7) [62-65].

![Diagram of self-condensing vinyl polymerisation](Image)

*Figure 1.7: Self-condensing vinyl polymerisation [61]*

Slow addition of monomer to a reaction mixture allows some control to be exerted in the synthesis of HBPs [63, 66]. The addition of a multifunctional core (as in dendrimer synthesis) to the reaction mixture has also been investigated [40-44]. In combination with slow addition of monomer this has been shown to allow the controlled synthesis of HBPs [41] with respect to molecular weight and polydispersity. The addition of a B₈ core, tris(2-aminoethyl)amine, to PAMAM HBPs [67] yields intrinsic viscosities that approximate more closely to Tomalia's dendrimers than in the absence of the core [68].
1.2.4 Properties of dendrimers and HBPs

1.2.4.1 Physical properties

Dendrimers and HBPs are not able to entangle via their polymer chains to the extent that linear polymers are. There is theoretically no entanglement at all in the case of the perfect dendrimer, as the molecules approximate Newtonian spheres [69, 70]. Therefore, the majority of polymer-polymer interaction is via the chain ends. Intrinsic viscosity increases approximately linearly with molar mass in the case of linear polymers, however for dendrimers and HBPs the curve is bell-shaped (figure 1.8) [3, 30, 71]. Beyond a certain generation number the intrinsic viscosity starts to decrease, the maximum marking the size at which the polymer first becomes globular. After this point the molecules can move easily with respect to each other. Hence, dendrimers and HBPs are considered to be low viscosity materials [70].

A comparison of the properties of linear, hyperbranched and dendritic aromatic polyesters [33] showed that the solubilities of the dendritic and hyperbranched materials were much greater than that of the linear polymer. Feast and Stainton have prepared a series of polyester dendrimers [72] that are all highly soluble in common organic solvents. In contrast their linear analogue, poly-p-hydroxybenzoic acid, is virtually insoluble in organic solvents.

![Figure 1.8: Intrinsic viscosity as a function of molecular weight for polybenzylether dendrons (•) polybenzylether dendrimers (■) and hyperbranched PAMAM (●) [30]](image-url)
A comparison of linear, hyperbranched and dendritic aromatic polyesters [33] concluded, surprisingly, that thermal properties such as \( T_g \) and onset of decomposition were independent of molecular architecture.

1.2.5 Applications

1.2.5.1 Applications of dendrimers

Much of the initial interest in dendrimer synthesis stemmed from their unusual structure [18, 20] that mimics some natural molecules. The subsequent investigation of their properties and potential usefulness [73] both uncovered many areas in which they might find application [28] and heightened interest in their more easily synthesised counterparts, hyperbranched polymers, with which they share many properties [3].

The interior of dendrimer molecules contains pores and cavities. These spaces and the easily modifiable surface functionality of dendrimers are exploited in many applications. A variety of biological applications has been identified [18, 74, 75]. Amphiphilic dendrimers can be used as encapsulation devices in a similar way to conventional micelles [76] and are used, for example, as drug carrier molecules. Other applications include, for example, the use of dendrimers as scaffolds for porphyrin arrays [77, 78].

Dendrimers can be used as modifiers to other polymer systems. The polyester dendrimers prepared by Feast and Stainton [72] have been blended with poly(ethylene terephthalate) and characterised in terms of their mechanical and dielectric properties. The first-generation dendrimer acted as a plasticiser, in contrast the second-generation dendrimer displayed antiplasticising behaviour. The use of dendrimers as resin modifiers is not nearly as common as that of HBPs. This may be due to the more cost- and time-efficient synthesis of HBPs [2, 3, 27, 79]. Synthesising dendrimers in large quantities is difficult and therefore their exploitation as resin modifiers has been limited [80].

1.2.5.2 Applications of HBPs

The lack of well-defined structure precludes the use of HBPs in some of the applications of dendrimers, largely biological and catalytic use [27], because of the
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structural sensitivity of such applications. HBPs find the majority of their applications in the fields of resin additives and coating components [27]. These materials are well suited to coating applications because of their high functionality, high solubility and low viscosity.

Thermosetting polymer resins with high temperature capability are brittle because of their high cross-link density. Conventional toughening agents, such as linear thermoplastics, tend to inhibit the processability of the system. The low viscosity, small size and potential for toughness enhancement of HBPs make them ideal candidates as resin modifiers [81]. The HBP surface can be functionalised in order to optimise the additive-resin interactions and so yield a molecular dispersion of additive that is not filtered out by the fibre mat during RTM [79]. The phase separation required for a toughening effect is induced subsequently [82-86] by changes in the solubility parameters of the resin and modifier during polymerisation. A secondary phase of around 1 μm has been shown to be the optimum particle size for enhancing resin toughness [81].

A large proportion of the published literature on the modification of resins with hyperbranched polymers focuses on the addition of hyperbranched polyesters to epoxy-amine systems [4, 79-91]. The use of the commercially available Boltorn additives, made by Perstorp Speciality Chemicals has been investigated in several studies [79, 80, 92]. These materials are hyperbranched aliphatic polyesters; both epoxy and hydroxyl functionalised materials have been blended with epoxy resins. The thermal and mechanical properties of resins modified with epoxy functionalised Boltorn hyperbranched additives have been measured [88].

An increase in fracture toughness of 100 % has been observed for a difunctional epoxy-amine system modified by the addition of 20 % epoxy functionalised HBP [4]. The modulus of the material is reduced by 10 % and the Tg by 15 K with respect to the unmodified resin. Carboxy-terminated butadiene acrylonitrile (CTBN) rubber (a conventional rubber toughening agent) proves less effective than the HBP, yielding a critical stress intensity factor ($K_{1c}$) of 1.07 MPa.m$^{1/2}$, compared to 1.21 MPa.m$^{1/2}$ for the HBP. CTBN also impairs the processability of the system owing to the higher viscosity of this material compared to the HBP (135 Pa.s for CTBN, 13 Pa.s for the HBP) [4].
Hydroxyl functionalised Boltorn additives have been blended with difunctional and trifunctional epoxy-amine systems at concentrations of up to 20 % by mass [80, 87]. The use of these additives increases the viscosity of the blend [80, 87] but this increase is smaller than that observed by the addition of rubber or thermoplastic toughening agents [30]. The impact strength of the difunctional resin increases by 100 % [87] and the trifunctional resin by 50 % [80] with the addition of 20 % by mass Boltorn additive.

1.2.6 Summary

The synthesis, properties and applications of dendrimers and HBPs have been reviewed. These materials possess a globular morphology and as such exhibit higher solubility and lower viscosity than their linear analogues. HBPs have less regular structures than dendrimers but may be synthesised more efficiently in terms of time and yield.

The major applications of dendrimers are in biological and catalytic fields, for which their perfect structure is necessary. HBPs are mainly used as resin additives, both for coatings and bulk materials. Whilst dendrimers would also be suitable for such applications, their expensive nature precludes their large-scale use. Therefore, the majority of the literature on resin modification with globular polymers concentrates on the use of HBPs. These additives have been shown to enhance the properties of matrix resins by enhancing toughness without significantly impairing processability, a goal not possible with conventional toughening agents.

1.3 Sol-gel synthesis of organic-inorganic hybrids

1.3.1 Sol-gel processing

The route most commonly used in the synthesis of organic-inorganic hybrid materials is the sol-gel technique [11]. This method can lead to the formation of materials in which the organic and inorganic components are intimately associated. This association imparts properties to the hybrid material that may be superior to
those of either individual component [12, 93]. The basis of the sol-gel technique is reviewed in detail in Brinker and Scherer's seminal book [11].

In its most common form, the sol-gel process involves the hydrolysis of a metal or metalloid alkoxide and its condensation to form a sol of oligomeric oxide species [11]. As condensation continues an amorphous three-dimensional network, the gel, is formed. The structure of the product is determined by the conditions under which the hydrolysis, condensation, drying and processing of the material are carried out [11, 94-97]. In this way control can be exerted over the physical properties, such as porosity and transparency, of the product [98].

The hydrolytic sol-gel route is well established [11], its basis in the case of silica is shown below (equations 1.1 to 1.3).

\[
\begin{align*}
\text{Hydrolysis:} & \quad =\text{Si-OR} + \text{H}_2\text{O} \rightarrow =\text{Si-OH} + \text{ROH} \\
\text{Alcohol condensation:} & \quad =\text{Si-OR} + \text{HO-Si=} \rightarrow =\text{Si-O-Si=} + \text{ROH} \\
\text{Water condensation:} & \quad =\text{Si-OH} + \text{HO-Si=} \rightarrow =\text{Si-O-Si=} + \text{H}_2\text{O}
\end{align*}
\]

This review will focus on the synthesis and applications of silicon hybrid materials, however, the use of other metal or metalloid elements in sol-gel processing has also been investigated [99].

1.3.1.1 History

Although major interest in nano-scale organic-inorganic hybrid materials has been apparent only in the last twenty years [11], sol-gel chemistry is not new. Silicon alkoxides were first produced over 150 years ago [100] by the reaction of silicon tetrachloride and alcohol. The compound was observed to gel on exposure to the atmosphere. However, potential applications for these materials (oxide films) were not identified until the 1930s [101].

A large increase in activity came at the start of the 1980s [11] with the recognition of the potential of hybrid materials as modified ceramics and the subsequent publication of a journal devoted to sol-gel materials [102]. At the start of this increase in activity commercial hybrid products were in the form of fibres [103] and coatings [104], the latter remaining their largest application [105].
1.3.1.2 The hydrolytic sol-gel process

A major advantage of the sol-gel technique over the conventional processing of oxide glasses is that it is a low temperature route, often being carried out at room temperature. This contrasts with the very high sintering (densification) temperatures (1200-2000 °C) [12, 13] traditionally required. The organic component of the hybrids would not be able to withstand such processing temperatures (500°C being an approximate limit for processing of the most thermally stable organics such as polyimides [12]).

The tetraalkoxysilanes most commonly employed in the sol-gel process are tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) [11, 13]. The hydrolysis and condensation of these alkoxysilanes is a more complex process than suggested by equations 1.1 to 1.3. The exact nature of the oxide product formed will depend on many factors [11, 94-97, 106]. These include the ratio of water to silane, the nature of the catalyst, the pH of the reaction mixture, the presence and nature of co-solvent, the temperature at which the reactions are carried out and the drying technique used. These many factors can make the reproducible sol-gel synthesis of materials difficult [99].

Water is required for the hydrolysis of alkoxysilanes (equation 1.1). However, the two liquids are immiscible so a homogenising solvent, commonly an alcohol, is also generally added to the reaction mixture. In the absence of a co-solvent hydrolysis can only occur at the interface between the TEOS and water [95]. The partially hydrolysed species are then able to enter the aqueous phase.

The hydrolysis of silicon alkoxides under neutral conditions is not rapid [93]. At neutral pH the gelation of TEOS takes several weeks. Therefore, a catalyst is employed which may be acidic, basic or nucleophilic. Most commonly mineral acids and bases are used, nucleophiles used are generally halide ions (fluoride ions are most effective) [94]. Under basic conditions condensation is fast compared to hydrolysis and dense, highly condensed colloidal materials will be formed [11, 95]. At low pH hydrolysis is fast relative to condensation, so less dense structures are formed [95].

In his comprehensive review of silica chemistry, Iler [107] divided the formation of silica into three regions according to pH. The boundaries of these regions are at pH 2 and pH 7. The point of zero charge and isoelectric point of silica both occur at
approximately pH 2. This point represents a maximum in the gel time versus pH profile [107] as uncharged species predominate and the rate of the hydrolysis process is slow. Between pH 2 and pH 6 the gel time steadily decreases as the species move further from their isoelectric point. Above pH 7 significant numbers of silica particles are negatively charged so the particles will repel each other and gelation will be disfavoured; silica dissolves above pH 11 [11, 108].

The structural unit of silica is the SiO$_4$ tetrahedron. The perfect silica structure is a three-dimensional network of corner sharing tetrahedra [94]. In practice, silica formed by alkoxysilane condensation is disordered [13, 109] as, largely due to steric constraints, condensation is incomplete [94]. Owing to incomplete condensation, silanol and possibly some alkoxysilane remain, leading to surface functionality of the material and the presence of pores in the gelled material. The optical, mechanical and electrical properties of the material are strongly affected by local structure [94].

The product formed by the thermal drying of sol-gel silica is known as a xerogel (Greek: xeros = dry) with a typical density of 1.2-1.3 g.cm$^{-3}$ [106]. If the liquid is removed from the reaction mixture under hypercritical conditions the network does not collapse and a very low density aerogel (Greek: aero = air) may be formed. The typical density of an aerogel is 0.1-0.3 g.cm$^{-3}$ [13].

### 1.3.2 Sol-gel hybrids

The area of sol-gel hybrids is a large and expanding one and as such many reviews [12, 93, 98, 99, 106, 110-122] of the field have been written. The potential of hybrid materials is great as they extend the range of available properties of both the organic and inorganic component because of the large area of interaction between the two phases [98]. Therefore, much research is being carried out into hybrid materials in which both phases consist of domains on a nano-scale. If at least one of the components of the hybrid is present on a scale of less than 100 nm, the material is considered to be a nanocomposite.

The mechanical, thermal, optical and chemical properties of hybrid materials synthesised by the sol-gel method are often enhanced with respect to simple blends of the inorganic component with the organic polymer [106]. The organic material may be chosen for properties such as its capacity to be functionalised,
processability or toughness. The inorganic may have the desirable properties of hardness, thermal stability and transparency [116]. By tailoring the ratio of organic to inorganic the properties of the resultant hybrid can be controlled.

Schmidt and co-workers [110, 123] carried out much of the initial research into the incorporation of organic material in the sol-gel process. Epoxy and methacryl monomers were linked to an alkoxysilane and cross-linked subsequent to the sol-gel reaction. The materials showed a homogeneous morphology, no porosity, no $T_g$ corresponding to the organic phase and good scratch resistance. Since these initial experiments, research into sol-gel hybrid materials has increased enormously as their potential applications have been revealed. Fewer than five publications on organic-inorganic hybrids were produced in 1985, whilst now many hundreds of papers are published each year [124].

1.3.3 Formation of sol-gel hybrids

The manner in which the organic and inorganic components of a hybrid material are associated has been classified [12, 93, 116]. For example, Novak [12] divided hybrid materials into 5 classes according to their structure and the manner in which the interact.

- Type I: The organic phase is a soluble, pre-formed polymer that is embedded in an inorganic network.
- Type II: The pre-formed organic polymer is bonded covalently to the inorganic network in which it is embedded.
- Type III: The organic and inorganic networks are mutually interpenetrating.
- Type IV: The organic and inorganic networks are mutually interpenetrating and are covalently bonded to each other.
- Type V: "Non-shrinking" sol-gel hybrids.

The organic and inorganic components of type I, III and V hybrids are held together by non-covalent interactions only (van der Waals, hydrogen or ionic [125] bonding). In type II and type IV materials there is covalent bonding between the organic and inorganic phases in addition to these weaker interactions [12].
1.3.3.1 Type I

The inorganic network is created around a pre-formed organic polymer (figure 1.9) [126]. In order to prevent phase separation a co-solvent must be found. The alcohol produced by hydrolysis of the alkoxysilane alters the solvent properties during the reaction. Therefore, an initially soluble organic polymer may precipitate during the reaction [12]. Such polymers include polyvinylpyrrolidinone [127].

![Figure 1.9: Type I hybrid, the inorganic network condenses around the pre-formed organic polymer [126]](image)

Type I hybrids have been formed by the *in situ* hydrolysis and condensation of TEOS/TMOS in a solution of a phenolic resin [128, 129]. The two phases interact by strong hydrogen bonding [129]. Strong hydrogen bonding between the phases has also been observed in polyacrylamide/TEOS [130] and polyurethane acrylate/TEOS materials [131].

1.3.3.2 Type II

In type II hybrid materials the organic and inorganic phases are covalently bonded to each other. The sol-gel reaction is carried out in the presence of a pre-formed organic polymer that has residual functionality. This allows it to react with the silica precursors and so become covalently bonded to the inorganic material.

A common example involves the reinforcement of an elastomeric polysiloxane with silica. This is achieved by the condensation of an alkoxysilane in the presence of an elastomeric phase such as polydimethylsiloxane (PDMS) [132]. Covalent bonds between the phases are formed by the participation of the PDMS alkoxy or hydroxy functionalised chain ends in the sol-gel reaction. Hybrids may be formed in an analogous manner [114] from polytetrahydrofuran.
1.3.3.3 Type III

Macroscopic phase separation is a common problem in hybrid synthesis. In some cases this problem may be overcome by the *in situ* polymerisation of both the organic and inorganic phases. If the right reaction conditions are employed it is possible to trap the organic polymer in the inorganic matrix before phase separation occurs. Examples of processes that can take place concurrently with the sol-gel reaction are the free radical polymerisation of vinyl groups and aqueous ring-opening metathesis polymerisation [126]. Concurrent sol-gel and radical polymerisations have been carried out in the synthesis of hybrids of 2-hydroxyethylmethacrylate and (3-methacryloyloxypropyl)trimethoxysilane [133].

1.3.3.4 Type IV

Covalent bonding between the two phases helps to inhibit phase separation during *in situ* polymerisation [134]. Hybrids of this type have been synthesised from 2-hydroxyethyl acrylate (HEA) and *tetraakis*(2-(acryloxy)ethoxy)silane by an HF catalysed sol-gel reaction [134]. The properties of these materials have been compared to those of HEA/TEOS hybrids in which inter-phase covalent bonds are not formed. Transmission electron microscopy (TEM) results suggest more mixing of the phases with less distinct phase boundaries in the presence of inter-phase covalent bonds.

1.3.3.5 Type V

Shrinkage during hybrid synthesis can be problematic as it may lead to sample cracking. Novak [126] has developed a method by which this shrinkage can largely be avoided by attaching the organic monomers to an alkoxy silane, in which the alkoxy group is polymerisable [126]. During the sol-gel reaction the alkoxy group is liberated as an alcohol and in the presence of the appropriate catalyst or initiator its polymerisation takes place.

1.3.3.6 Alternative classification

A commonly used method of classification [93], which has largely superseded the Novak classification [12], distinguishes only between materials in which only weak interactions exist (class I, encompassing types I, III and V) and those in which there is covalent bonding between phases (class II, encompassing types II and IV).
Hybrids may be classified according to the morphology of the material obtained. This may be homogeneous [135], derived from monomers with both organic and inorganic functionality, or from miscible individual components, or heterogeneous phase separated systems [136].

Sol-gel hybrid materials have been given various names including ormosil (organically modified silicate) [123], ormocer (organically modified ceramic) [137] and ceramer [138].

1.3.3.7 The rôle of the catalyst

The sol-gel process may be catalysed by acids, bases or nucleophiles (commonly $F^-$) [139, 140]. Acids and bases are generally chosen to be volatile in order to facilitate their removal at the end of the reaction [141]. The catalyst chosen will affect the morphology of the product; acid catalysts tend to give rougher surfaced products that have a lower degree of condensation than basic catalysts [142].

A study into the effect of the catalyst on the product of the sol-gel reaction of TEOS and $N$-$\beta$-aminoethyl-$\gamma$-aminopropyltrimethoxysilane (1.1) has been carried out [143]. Materials were synthesised using either hydrochloric acid or ammonium hydroxide as the catalyst. In the case of acid catalysis the condensation of the silanol groups was more rapid, leading to larger particles than the basic catalyst.

![Diagram of N-$\beta$-Aminoethyl-$\gamma$-aminopropyltrimethoxysilane](1.1)

![Diagram of GPTMS](1.2)
Boron trifluoride diethyl etherate can act as a catalyst to both the silica sol-gel reaction and the polymerisation of epoxy groups [144, 145] (figure 1.10). Therefore, it is an ideal catalyst for the synthesis of hybrid materials based on the precursor 3-glycidoxypropyltrimethoxysilane (GPTMS) (1.2) acting as both the organic and inorganic component. High concentrations of the catalyst favour the formation of the inorganic network and so can sterically inhibit the formation of organic chains. Therefore, by adjusting the catalyst concentration, tailoring the composition of the hybrid product is possible.

![Figure 1.10: Epoxy ring opening using a boron trifluoride catalyst [145]](image)

**1.3.4 Single-component precursors**

It is possible to prepare single phase organic-inorganic hybrid materials in which the organic component (which is not polymeric) is covalently bonded to the precursor of the inorganic phase [146]. The most common example of this type of hybrid is formed by the hydrolysis of a mono- or disubstituted alkoxysilane, i.e. Si(OR)_{4-x}R'_x (x=1 or 2). R'-Si is non-labile, whilst Si-OR is hydrolysable [93]. Such materials were initially investigated by Schmidt [137] in order to reduce the cross-link density of the sol-gel product (by the presence of the organic) and hence improve their resistance to abrasion.

A study into the effect of alkyl group on the textural properties of the hybrids has been carried out [147]. On increasing alkyl chain length the surface area and total pore volume decreased, whilst microporosity increased. Increasing the chain length of the alcohol used as a solvent increases the specific surface area of the material [148].
The ratio of organic to inorganic material in these sorts of hybrids can be tailored by the use of two precursors, e.g. \( a\text{Si(OR)}_{4+x}R'_x \) and \( b\text{Si(OR)}_4 \) \([149]\). Varying the value of \( a \) with respect to \( b \) will affect the proportion of inorganic material in the hybrid product \([112]\).

### 1.3.4.1 Coupling agents

Substituted alkoxysilanes containing an organic functional group are commonly employed in the synthesis of hybrids \([131, 133-136, 144, 150-156]\). The molecules are of the generic nature \((\text{RO})_3\text{Si-X-A}\), in which \( A \) represents the organic functional group and \( X \) is a spacer group, commonly an ethyl or propyl chain, for example 3-aminopropyltriethoxysilane \((1.3)\) \([150]\) or GPTMS \((1.2)\) \([151]\). This type of material finds application both as the precursor in its own right \([157]\), or as a mediator between the organic and inorganic phases \([156]\).

(1.3): 3-Aminopropyltriethoxysilane

The formation of silica hybrids of poly(2-hydroxyethylmethacrylate) with and without the coupling agent 3-methacryloxypropyltrimethoxysilane has demonstrated its rôle in enhancing the interpenetration of the organic and inorganic phases \([154]\). Coupling agents with both methacrylate and silane functionality have been shown to enhance the mechanical properties of a hybrid material by increasing interaction between the phases \([158]\).

### 1.3.4.2 Bridged precursors

If the organic group is bonded to two or more alkoxysilanes it will be incorporated into the matrix as a spacer \([93, 98, 135, 146]\) (figure 1.11).

**Figure 1.11: Bridged precursor [135]**
Initially, arylene-bridged materials were investigated in order to examine the effect of rigid spacers on the sol-gel material [159]. A wide range of bridging organic components can be employed and their properties can be varied in terms of length, flexibility, geometry and functionality (figure 1.12) [117, 135, 160].

1.3.5 The organic phase

1.3.5.1 Elastomers

Elastomeric polysiloxanes, such as PDMS [132], are commonly reinforced by silica using a sol-gel method (figure 1.13) [161] in order to enhance their, generally rather poor, mechanical properties. The sol-gel route to reinforcement can lead to hybrids with superior mechanical properties to those formed by direct blending [162]. Many other rubbers such as polybutadiene [163], polymethylacrylate [164] and poly(propylene oxide) [165-167] can also be toughened using this route.

Mark et al. [132, 162] used TEOS to reinforce hydroxyl-functionalised PDMS. The silica domains formed are typically a few nanometres in diameter [132]. Covalent bonds between the two phases form by the participation of PDMS hydroxy or alkoxy chain ends in the sol-gel reaction.

Toughened elastomers made by sol-gel methods have been used as polymer resin modifiers [168]. The in situ formation of such a hybrid has led to the successful toughening of a high temperature polymer, poly(biphenyl ether triphenyl phosphate). The resultant hybrid shows enhanced toughness and extensibility, an addition of 8 weight % of the rubbery phase giving a five-fold increase in toughness [168].
1.3.5.2 High performance polymers

Much work has been carried out on the synthesis of hybrids based on polyimides, due to their high temperature capability [169, 170]. These polymers are used in microelectronics applications [171] and in composite materials [106]. The organic polyimide phase is often formed from a polyamic acid precursor [169]. Alternatively, an oligomeric isoimide may be employed as the organic precursor [172, 173]. The silica and polyimide phases of the hybrid may be compatibilised by the use of a coupling agent [136, 171, 172, 174-176], e.g. the addition of GPTMS (1.2) [177] and TEOS to an ethanol solution of polyamic acid [136, 178].

A co-continuous morphology imparts high thermal stability [172, 179] and a low coefficient of thermal expansion to the material, whilst a morphology consisting of particles in a matrix will enhance the strength and ductility of the polyimide [178, 180]. Examples of other high performance polymers used in hybrids include aromatic polyamides [181] and silsesquioxanes [182].

1.3.5.3 Other polymers

Sol-gel hybrids of Nafton have been synthesised [183-187]. In general, the use of fluoropolymers has been slight [115] owing to the fact that they generally only dissolve in perfluorinated solvents and these are highly incompatible with water.

The properties of cellulosics [126, 188] may be enhanced by the incorporation of a sol-gel inorganic phase. Optically transparent hybrids have been formed using cellulose acetate at 2 to 85 weight %.
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1.3.6 Hybrid particles

The majority of research into sol-gel hybrids has the aim of forming a thin film or monolith. More rare is the use of sol-gel techniques in the synthesis of particulate products [189, 190].

Purely inorganic silica particles are commonly synthesised following the method reported by Stöber, Fink and Bohn [191]. This method involves the hydrolysis of a tetraalkoxysilane in a solution of water and alcohol at high pH. The basic nature of the reaction mixture and the high ratio of water to tetraalkoxysilane (typically 20:1 or greater) both favour the formation of compact particles as opposed to a macroscopic network [11]. Varying the concentration and nature of the reactants and the reaction temperature allows control to be exerted over the diameter of the resultant particles [191-195].

Organically modified silica nanoparticles have been synthesised as an emulsion in oil, stabilised by surfactants [196-198]. The hydrophobic organic groups will tend to be at the periphery of the particles, interacting with the oil and thus stabilising the particles. Hybrid MCM-41 type nanoparticles have been synthesised via a sol-gel route [199], a trialkoxysilane precursor being added to the silica source.

The sol-gel method may be used to synthesise hybrid particles in which the organic component is a labile template [200]. Removal of the labile organic component subsequent to the sol-gel reaction yields porous particles.

Pre-formed silica particles may be coated with hybrid precursors [190], RₙSiOR₄₋ₙ, which are then hydrolysed and condensed to form a polyorganosilane layer. TEOS and methyltriethoxysilane have been added to a commercial silica sol in order to form core-shell particles [201]. The presence of the surface methyl groups reduces the particle-particle interaction.

Alternatively, hybrid core-shell particles may be synthesised by precipitating silica around a pre-formed organic polymer. Micron-scale hybrids have been formed by the hydrolysis and condensation of TEOS in the presence of polystyrene particles, which act as seeds for the formation of silica [202]. The emulsion polymerisation of styrene with 3-trimethoxysilylpropylmethacrylate [203] leads to silane-functionalised
particles that are then able to interact with a tetraalkoxysilane. Hydrolysis and condensation yield particles with a 40 nm thick silica shell.

PDMS droplets have been encapsulated by a sol-gel method [204]. An aqueous emulsion of PDMS is formed at high pH. The droplets are then coated in a thin silica shell by the addition of a saturated sodium silicate solution. The thickness of the shell is increased by the addition of TEOS and ethanol.

1.3.7 Characterisation

1.3.7.1 Composition and structure

Many common analytical techniques have been applied to the characterisation of hybrid materials. These include water titration [93], elemental analysis [144], mass spectrometry [93] and many spectroscopic techniques including infrared (IR) [127, 144], ultraviolet (UV)-visible [154] and nuclear magnetic resonance (NMR) [144] spectroscopies.

Solid state NMR spectroscopy is commonly used to study the miscibility, intermolecular interactions and morphology of hybrid materials [205]. $^{29}$Si NMR spectroscopy can be used to measure the degree of condensation of silica in a hybrid material by analysing the relative intensities of the peaks corresponding to silicon atoms connected to 0, 1, 2, 3 or 4 bridging oxygen atoms [11, 160]. A quaternary silicon atom, bonded to four oxygen atoms is designated a Q species, a tertiary silicon atom, bonded to three oxygen atoms is a T species. A fully condensed, unsubstituted silica species is designated Q$^4$ [205] (figure 1.14) and will appear at a particular chemical shift in the $^{29}$Si NMR spectrum. An increased degree of condensation (e.g. from Q$^0$ to Q$^4$) generally results in an upfield shift in the NMR spectrum. The detection of other nuclei, e.g. $^{13}$C [98] or $^{17}$O [149, 206], can also aid in the elucidation of hybrid structure.

The sol-gel reactions of TEOS with methyltriethoxysilane, ethyltriethoxysilane and phenyltriethoxysilane have been followed by $^{29}$Si NMR spectroscopy [207]. The degree of cross-condensation (i.e. a TEOS species condensing with a triethoxysilane species) could be determined from the NMR spectra.
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Figure 1.14: Quaternary (Q) silica species

Fourier transform IR (FTIR) spectroscopy can be used to characterise the structure of hybrid materials [208], including the interactions between the organic and inorganic phases [136]. The presence of silica in a sample can be confirmed by the presence of two characteristic absorptions, Si-O-Si asymmetric stretching at around 1100 cm\(^{-1}\) [127] and a band around 800 cm\(^{-1}\) showing the presence of a silica network [129, 207].

FTIR and Raman spectroscopy have been used to study the sol-gel reaction of GPTMS (1.2) and 5,6-epoxyhexyltrimethoxysilane [209-211]. These studies show that the reaction pathway depends on the ratio of alcohol (methanol) to water employed (figure 1.15).

Figure 1.15: Possible ring-opening reactions of GPTMS [209]
1.3.7.2 Morphology

Scanning electron microscopy (SEM) [205], TEM [212] and atomic force microscopy (AFM) [213] have been used to determine the morphology of hybrid materials. Microscopy can reveal whether the sample is homogeneous [213] or heterogeneous [150], and if it is heterogeneous can show the dimensions, distribution and morphology of the phases. Sample homogeneity can also be elucidated by light scattering studies, low values indicating high homogeneity [110]. AFM can be used to produce three-dimensional images of the surface of a sample, with sub-nanometre resolution [127]. Energy-dispersive X-ray (EDX) analysis can be used in conjunction with SEM in order to show the distribution of silicon atoms in the sample [136, 214]. Sample surface area is measured by nitrogen sorption porosimetry using the Brunauer-Emmett-Teller (BET) method [110].

Small angle X-ray scattering (SAXS) analysis can be used to examine surface roughness [98], morphology [133, 215] and particle size [216]. Time-resolved SAXS has been used to study the reaction kinetics of gel formation [216]. The wide angle X-ray diffraction (WAXD) pattern of a material can be used to yield information on the crystallinity of a hybrid [127]. In the case of crystalline organic polymer, the WAXD pattern will show its characteristic peaks.

1.3.7.3 Rheology

The viscous flow of an organic polymer, for example poly(vinyl formate) [115], can be eliminated by the presence of a confining silica phase. In this case the glass transition of the organic material is broadened and is at higher temperature than for the pure organic polymer.

The rheology of a methanol solution of phenolic resin and TMOS during gelation has been studied [128]. It was found that altering the reaction conditions could control the gel time. Gelation could be accelerated by increasing the reaction temperature, increasing the concentration of both TMOS and the phenolic resin, the water:TMOS ratio and the pH of the reaction [128].

1.3.7.4 Thermal properties

The thermal decomposition of hybrid materials is measured by thermogravimetric (TG) analysis [98, 217]. The presence of silica can increase the degradation
temperature of a hybrid with respect to the pure organic polymer, e.g. for silica reinforced PDMS [218], polyimide [169] and polyethersulfone [217].

The thermal stability of hybrid materials formed by the sol-gel condensation of various single-component alkoxysilane precursors has been studied by TG analysis [219]. The gel obtained from TEOS shows a mass loss at 80 °C, due to further condensation, but no further mass loss on heating to 1000 °C. The substituted alkoxysilanes all show a mass loss due to degradation of the organic material.

Differential scanning calorimetry (DSC) may be used to determine T_g, melting point and degree of crystallinity of hybrid materials [113, 220]. DSC has also been used to demonstrate homogeneity [221]. The single-phase morphology of a polyethyloxazoline-silica hybrid has been inferred from the absence of the glass transition of the organic polymer in the DSC spectrum.

The presence of a coupling agent has been shown to increase the T_g (by DSC) of poly(2-hydroxyethylmethacrylate)/silica hybrids [154, 222] and of polyimide/silica hybrids [176]. TG analysis has shown the increase in thermal stability of poly(vinyl acetate)/silica hybrid materials, due to the incorporation of a silane coupling agent in their synthesis [152].

The fire retardance of polyimides has been enhanced by the incorporation of silica using sol-gel processing [223].

1.3.7.5 Mechanical properties

The reinforcing ability of silica has been demonstrated in many different materials [131, 133, 224-227]. The stress-strain behaviour of some hybrid materials, for example polyvinyl formate/silica, has been shown to be different to that of either component [115], with hybrid materials achieving much higher energy-to-break values. The compressive strength of polymethylmethacrylate (PMMA)-silica hybrids has been shown to increase linearly with the volume fraction of silica present [224], from 81 MPa for pure PMMA to 545 MPa for pure silica.

The mechanical properties of methacrylate/silica coating materials have been investigated [228]. The mechanical properties were found to be independent of coating thickness. In general, both hardness and elastic modulus increase with silica content.
The tensile strength of poly(vinyl acetate) has been increased by the incorporation of silica [226]. The maximum tensile strength (30 MPa) is observed with the addition of TEOS at 50 weight %. The incorporation of a silane coupling agent further increased the tensile strength to 50 MPa [226]. The use of a coupling agent has also been shown to enhance the mechanical properties in the case of polyurethane-acylate hybrids [131].

### 1.3.8 Dendrimer hybrids

A major application of dendrimers in sol-gel materials is as pore templates, because of their spherical morphology. Pyrolysis of the hybrid material allows removal of the organic template [229], leaving a porous silica product. The pore size generally shows a correlation with the size of the dendrimer template [229, 230]. The dendrimer most commonly used is a PAMAM (figure 1.16) [40]. PAMAM is mixed with a silane precursor; hydrolysis and condensation proceed, leading to a product consisting of the dendrimer dispersed in a silica matrix [231]. This hybrid material finds its major application as a catalyst support [232].

![Figure 1.16: Example of a second generation PAMAM dendrimer [40]](image)

Typically, TEOS [231] or TMOS [233], with [231, 234] or without [235, 236] a coupling agent, is used as the inorganic precursor. For example, the surface amine groups of the PAMAM dendrimer can react with the epoxy functional groups of
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GPTMS (1.2), leading to a silane functionalised dendrimer [234]. TEOS is then added and the sol-gel reaction carried out (figure 1.17). The hybrids showed enhanced thermal stability with respect to the pure organic polymer, increasing with concentration of GPTMS. SEM reveals phase separation in the absence of the coupling agent [235]. Zero generation PAMAM is able to toughen silica gel derived from TMOS [233]. The rupture strength of the hybrid is 41.6 MPa, compared to 32.9 MPa in the absence of the organic polymer.

![Figure 1.17: Formation of the hybrid from silane modified PAMAM dendrimer and tetraalkoxysilane [231]](image)

The use of carbosilane dendrimers in sol-gel processing has been investigated. For example, a vinyl-terminated carbosilane dendrimer is reacted with a triethoxysilane to impart (RO)₃Si- functionality to the surface of the polymer. Carbosilanes assemble during sol-gel processing to form a porous network [237]. These materials find application as coatings, catalyst supports and porous membranes [238].

Dendrimer-like 'star gels' have been used as single component precursors to hybrid materials [115]. They typically consist of an organic core with three or four flexible chains, terminating in alkoxyisilane groups (figure 1.18) [115]. The hybrid products are tough, transparent glasses. They exhibit elastic behaviour at stresses of up to 350 MPa.
1.3.9 Hybrid/epoxy blends

Sol-gel materials have been blended with epoxy resins. The *in situ* formation of the inorganic phase can lead to increased thermal stability compared to the conventional blending of epoxy resins with pre-formed filler particles [239]. Thermal and mechanical properties have also been enhanced in some cases [240-243].

An epoxy/silica hybrid has been formed by the addition of GPTMS (1.2) to a difunctional epoxy prepolymer [240, 244] and its *in situ* hydrolysis and condensation. The monomer is cross-linked by the addition of a primary [240, 244] or tertiary [244] amine curing agent. The thermal and mechanical properties of the resin were significantly improved in the case of the primary amine but not for the tertiary amine. The primary amine cured material is homogeneous, whilst the tertiary amine cured system is heterogeneous, the different morphology is due to the different cure mechanisms involved. FTIR spectroscopy [244] shows that, in the case of the primary amine, a covalent bond is formed between the silanol groups of hydrolysed GPTMS and the hydroxyl groups of the opened epoxy rings, hence giving a strong interface between the phases. Kinetic studies of the sol-gel reaction of GPTMS (1.2), as a model compound for epoxy/silica hybrids, have been carried out [245-247]. The addition of an amine to GPTMS catalyses both its sol-gel reaction and the ring opening of the epoxy group [157].

The incorporation of silicon and phosphorus into a difunctional epoxy resin by a sol-gel method has increased the flame retardance of the epoxy (figure 1.19) [248-250]. The addition of a coupling agent prior to TEOS can enhance the interaction between the organic and inorganic phases [251]. TEOS and a phosphorus-containing silane were then added [248]. Whilst the flame retardance of the epoxy was increased by
the additives their thermal stability was reduced. The activation energy for the thermal degradation of the hybrids was reduced from 282 kJ.mol\(^{-1}\) for the pure epoxy, to 116 kJ.mol\(^{-1}\) for the hybrid \([249]\). It was suggested that this was due to the P-C bonds present acting as weak links.

![Polymer chain]

**Figure 1.19: Synthesis of silicon and phosphorus containing epoxy hybrid \([248]\)**

The difunctional epoxy diglycidyl ether of bisphenol A (DGEBA), cured with the aliphatic amine Jeffamine D-2000, has been reinforced by the addition of TEOS \([241, 242, 252, 253]\). Addition of TEOS to yield 10 vol % silica in the hybrids leads to an increase in the storage modulus of the material by two orders of magnitude \([241, 253, 254]\).

The interaction between the organic and inorganic phases may be tailored by surface modification of the silica particles \([255]\). Epoxy or amine modification has been shown to increase the interphase interaction, leading to an increase in \(T_g\) and decrease in damping as the particle concentration is increased.

### 1.3.10 Applications

#### 1.3.10.1 Abrasion resistant coatings

Sol-gel hybrid materials are used as coatings for metals \([256-258]\), polymeric materials \([259, 260]\) and other materials such as stone \([261]\). The coatings combine the flexibility of the organic component with the hardness of the inorganic component \([259]\).
Ceramic materials are, in general, more resistant to oxidation, corrosion, erosion and wear than metals [256, 262]. Therefore, the use of sol-gel hybrid materials as corrosion [257] and abrasion [263] resistant coatings for metal has proved successful. Mild steel substrates have been spin coated with hybrid sols and the silica films shown to act as a protective barrier against wet corrosion of the metal [256]. Other metals successfully coated in this way include aluminium, zinc and magnesium [257]. The high corrosion inhibition can be attributed to the good adhesion between the coating and the substrate, due to the formation of covalent bonds between surface hydroxyl groups of the metal and the added silicon alkoxide [257]. This good adhesion eliminates the need for chemical pretreatment of metal surfaces [257, 258]. Metals coated in this way find application in fields such as the automotive and aerospace industries [257].

Polymeric materials [260, 264, 265] have also demonstrated increased abrasion resistance after the application of sol-gel coatings. For example GPTMS-based hybrids have been used as a coating for polyethyleneterephthalate and polycarbonate [259]. The coatings display good adhesion to the substrates, abrasion resistance and flexibility.

Coating materials that are UV-curable have been developed [266, 267], in order to overcome lengthy thermal curing processes. Acrylate-functionalised organic polymers [267], or molecules combining acrylate and silane functionality [266], are combined with an inorganic phase.

1.3.10.2 Decorative Coatings

Sol-gel materials exhibit good adhesion to glass substrates owing to their ability to react with the surface silanol groups; hybrids have been employed as decorative coatings for glass [262, 268, 269]. Sol-gel techniques have been used to produce lead and fluorine free white paints [269]. In the case of lead crystal glass, lead will slowly leach out into liquid in contact with the glass. A sol-gel hybrid coating can provide a diffusion barrier against this process [268].

1.3.10.3 Sensors

Using sol-gel techniques active organic molecules can be incorporated into a matrix to yield optical, electrochemical, thermal or radiation sensing devices [270, 271].
Most organic-inorganic hybrids are insulating materials and must be coupled to other materials in order to be exploited in electrochemical applications. Hybrid materials can be used in the chemical modification of electrodes as they exhibit mechanical stability and durability, structural rigidity and the possibility for molecular discrimination. Hybrid materials are used in electrochemical applications, including spectrochemical devices and electrochemical biosensors [270, 272]. Organically modified silicates are widely used in electroanalysis, e.g. in coatings with selective permeability, electrocatalysis and detectors for chromatography [270, 272].

The use of sol-gel hybrids in both passive and active optical applications has been investigated [262, 271, 273]. Sol-gel materials have been shown to have potential as host photonic materials [274, 275]. The unmodified ormosil networks have low optical attenuation in the desired spectral region and so can be used as short photonic waveguides for passive optical transmission [274, 276, 277].

Doped sol-gel matrices can be used in active photonic devices [274], for example in frequency doubling, electro-optical modulation [278], optical data storage [279] and as luminescent coatings [280]. The advantages of sol-gel matrices as hosts for optically active additives are excellent optical activity, good thermal stability, control of refractive index, ease of fabrication [278] and their non-leachable nature [280].

A variety of sol-gel electrochromic and photochromic films have been developed. Electrochromic films find application in optical displays; photochromic films are used, for example, as sensors of ultra-violet radiation and switching devices [271, 281].

1.3.10.4 Structural materials

Sol-gel hybrids have found application not only as coatings but also in bulk materials [262]. Rubbers, including poly(acrylonitrile-co-butadiene) [282] and PDMS [113], and glassy thermosetting polymers such as polyimides [283] have been reinforced in this way [113]. Applications include enhancing the thermal and mechanical properties of matrices for carbon fibre composites [283] and strengthening dental composites [284-286].
1.3.11 Alternative sol-gel techniques

1.3.11.1 Non-aqueous sol-gel reaction

The hydrolysis and condensation of tetraalkoxysilanes can be carried out using methanoic acid as the catalyst, solvent and water source for the reaction. Methanoic acid is a solvent for many organic polymers [287, 288]. An example of such a process is the synthesis of a hybrid from polyaniline and TEOS [289]. A transparent monolithic hybrid product has been produced using this method [289].

1.3.11.2 Emulsion method

Hybrid materials may be prepared from emulsions of the precursors [290]. Microhybrid materials have been synthesised from a mixture of an aqueous emulsion of urethane acrylate monomers and hydrolysed TEOS [127, 131]. The tensile strength of the material increases with increasing silica content up to the point of phase separation [127]. An emulsion method has also been used to synthesise hybrids of poly(butyl methacrylate) [101].

1.3.11.3 Non-hydrolytic sol-gel method

The non-hydrolytic sol-gel (NHSG) route to the synthesis of organic-inorganic hybrids is less well-established than the hydrolytic technique and applications for the materials are almost totally unexplored [276]. The NHSG method involves the reaction of a silicon halide [291-294] (other inorganic species including aluminium, titanium and zirconium [295-298] and binary systems [299-301] have also been investigated) with an oxygen donor to form an inorganic oxide under non-aqueous conditions (figure 1.20).

The oxygen donor is commonly an alkoxide [293], ether or alcohol [292]. The reaction is catalysed by a Lewis acid, most often iron(III) chloride; the metal of the catalyst is incorporated into the product and so can lead to a coloured product [291]. Many of the precursors are liquid and so the process is often solvent-free [293].
Two sets of experimental conditions for the process have been developed. The first involves the use of sealed tubes at autogenous pressure [291], the second is carried out at ambient pressure under a flow of nitrogen [293]. Both processes are typically carried out at temperatures of 85-110 °C.

The hydrolytic and non-hydrolytic sol-gel processes are compared in table 1.1 [302].

<table>
<thead>
<tr>
<th>Hydrolytic</th>
<th>Non-hydrolytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Facile, low temperature process</td>
<td>Facile, low temperature process</td>
</tr>
<tr>
<td>Homogenising solvent used</td>
<td>May be solvent-free</td>
</tr>
<tr>
<td>Water required</td>
<td>Suitable for water-sensitive reagents</td>
</tr>
<tr>
<td>Water and alcohol formed</td>
<td>Alkyl halide formed</td>
</tr>
<tr>
<td>Suitable for ionic and oxygen-containing species</td>
<td>Oxygen-containing species may cause side reactions</td>
</tr>
<tr>
<td>Limited compatibility with hydrophobic species</td>
<td>Hydrophobic species not problematic</td>
</tr>
<tr>
<td>Well established</td>
<td>Comparatively new technology</td>
</tr>
</tbody>
</table>

Table 1.1: Comparison of hydrolytic and non-hydrolytic sol-gel processes [302]

1.3.12 Inorganic phases other than silica

In addition to silica, the sol-gel syntheses of alumina [303], titania [304, 305] and zirconia [304], and hybrids of these materials [113, 306], have been investigated.

Titania can provide reinforcement to organic polymers [307, 308]. It has been used in PDMS hybrids in place of silica, as at high temperature the residual silanol groups could cause degradation of the polymer [309]. Aramid/titania hybrids have been synthesised [308]. If the aramid chains are silane functionalised, the tensile strength is observed to increase with increasing titania content [308].
Zirconium butoxide is commonly used as a precursor to zirconia sol-gel materials [310, 311]. For example it is employed, with cellulose acetate, in the synthesis of gel fibres for the immobilisation of the enzyme invertase [311]. The thermal stability of trapped invertase is increased with respect to the free material.

Alumina has been employed in the synthesis of few hybrid materials. The incorporation of an alumina phase into an organic polymer has been shown to decrease the thermal stability of the polymer [312].

1.3.13 Summary

The sol-gel technique represents a low-temperature route to the inorganic modification of organic polymers. The combination of organic and inorganic material can have a synergistic effect, allowing the desirable properties of the phases to be simultaneously expressed. Improvements in properties such as high temperature performance and strength, together with substantial reductions in flammability and thermal expansion behaviour compared to a purely organic material have been achieved.

Currently, the major application of sol-gel hybrids is in coatings. However, a variety of other uses have been identified, including sensing devices and structural materials. Sol-gel hybrids, as additives to matrix resins, have the potential to enhance the physical properties of composite materials.

1.4 Aims

The ultimate objective of the project was the development of a polymer matrix for structural composites having enhanced thermal and mechanical properties compared to current systems, whilst maintaining easy processability.

In the pursuit of this objective, an investigation into the potential of dendrimers and hyperbranched polymers as resin additives was carried out. These materials have the potential to act as both toughening agents and rheology modifiers. The synthesis of sol-gel hybrid particles was also investigated, as it was hypothesised that the incorporation of inorganic material into an organic matrix may enhance its thermal
properties and that this benefit may be greatest when the two phases are interconnected on a nano-scale. The specific aims are listed below.

- To develop a resin system that is tough. The epoxy system most commonly used in aerospace applications is tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), blended with 4,4'-diaminodiphenylsulfone (DDS). The value of $K_{1c}$ for this system is 0.5 MPa.m$^{1/2}$; with the addition of a conventional high-performance toughening agent (PES) $K_{1c}$ values of 1.4 MPa.m$^{1/2}$ have been observed [2]. It was hoped to achieve a similar value of toughness in a more easily processable system.

- To achieve this toughness in a low-viscosity resin system. Ideally, the resin should be of appropriate viscosity for use in infusion techniques such as RTM. The preferred viscosity at the injection temperature for RTM resins is 100 to 500 mPa.s [313].

- To achieve a thermally stable system. Structural components for aerospace applications must be able to withstand high temperatures long term. For example, the Eurofighter Typhoon has a lifetime of 6000 flying hours [314]. Its exterior surfaces reach temperatures of around 120 °C, due to aerodynamic heating. TGDDM/DDS has a $T_g$ of 262 °C and so can withstand such temperatures. The system developed should be sufficiently thermally stable to be used long-term at temperatures of at least 120 °C.

- To synthesise nano-scale organic-inorganic hybrids and to assess their potential as resin additives in the fulfilment of the above aims. Nano-scale may be defined as having at least one phase dimension that is less than 100 nm. The hybrids formed should be particulate so they can be dispersed in a matrix resin. Therefore, the use of a dendrimer or hyperbranched polymer as the organic phase will be investigated because these materials have a globular, non-entangling morphology.

1.5 References

Chapter 1: Introduction

[34] Y.H. Kim and O.W. Webster, Macromolecules, 1990, 23, 4726
Chapter 1: Introduction

[59] L.J. Hobson and W.J. Feast, Polymer, 1999, 40, 1279
Chapter 1: Introduction


D.A. Tomalia, V. Berry, M. Hall and D.M. Hedstrand, Macromolecules, 1987, 20, 1164


L. Boogh, B. Pettersson, P. Kaiser and J-A.E. Manson, SAMPE J., 1997, 33,


D. Ratna and G.P. Simon, Polymer, 2001, 42, 8833

R. Mezzenga, B. Pettersson and J-A.E. Manson, Polymer, 1999, 40, 2249


D. Ratna and G.P. Simon, Polymer, 2001, 42, 8833

R. Mezzenga, L. Boogh and J-A.E. Manson, Polymer, 2001, 42, 8833

R. Mezzenga, L. Boogh and J-A.E. Manson, Polymer, 2000, 41, 1456


R. Mezzenga, L. Boogh, B. Pettersson and J-A.E. Manson, Polymer, 1999, 40, 2249


Chapter 1: Introduction

[191] W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62


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[307] X.P. Zhao and X. Duan, J. Colloid Interface Sci., 2002, 251, 376
Chapter 2: Hyperbranched polymers as resin modifiers
2.1 Introduction

2.1.1 Toughness enhancement

Although many factors are known to contribute to composite performance under impact loading conditions, the nature of the matrix phase is recognised as having a significant bearing on the ultimate damage tolerance characteristics of the material. As a result, substantial effort has been devoted to the topic of bulk polymer toughness enhancement with a view to improved damage tolerant composite materials.

In many aircraft composite applications TGDDM, a tetrafunctional epoxy with the potential to exhibit a high $T_g$, has been employed [1, 2]. This is due to a variety of benefits that such materials exhibit in comparison to other polymers and therefore epoxy resins currently form the basis of most structural adhesive and composite matrix resin formulations. Despite exhibiting substantial elevated temperature capabilities, such highly cross-linked polymers are usually brittle. Therefore, toughness enhancement is considered important.

The well-known technique of rubber modification is extremely efficient in promoting toughness enhancement in relatively low cross-link density polymers. However, it is of little value with high cross-link density polymers such as the tetrafunctional systems mentioned above. The presence of the rubber phase toughens by plasticisation at phase boundaries due to mixing of matrix resin and additive, and by cavitation of the rubber particles. Plasticisation aids in the dissipation of fracture energy as the stress yielding and resultant plastic deformation consume energy; cavitation lowers the constraint in the vicinity of the voids and so promotes shear yielding [3, 4].

High functionality resins cannot be toughened by this method as the rigid, densely cross-linked matrix resin inhibits plastic deformation; therefore sufficient fracture energy cannot be dissipated in this manner to retard crack propagation. Toughening by thermoplastic modification is effective in these resin systems [1, 2, 5]. It has been demonstrated that the thermoplastic must often be added at a sufficient concentration to form a co-continuous morphology in order for toughening to be achieved [1, 2, 6]. The ductile thermoplastic phase is able to deform plastically in the vicinity of the crack tip. Fracture energy is transmitted through the thermoplastic,
with the effect of toughening the blend with respect to the unmodified thermoset. However, the addition of such a thermoplastic to an epoxy resin causes a dramatic increase in viscosity [2] rendering the system inappropriate for low cost manufacturing techniques.

The three major strategies employed for the toughening of thermosetting resins are described below.

2.1.1.1 Rubber toughening

Rubbers are commonly used to toughen epoxy systems; 5 to 20 % of a suitable rubber, such as CTBN (2.1), is added to the resin. During cure, phase separation occurs to leave rubber particles embedded within the matrix [3]. Rubbers toughen epoxy resins by increasing the extent to which energy dispersing deformations can occur as described in section 1.1 above. Although successful for difunctional epoxy systems, rubber toughening is less useful in high cross-link density resins, typical of those used in aerospace applications. In addition, the relatively low thermal stability of the rubber component can cause problems, such as loss of mechanical properties at elevated temperatures [1, 5, 7].

![CTBN structure](image)

(2.1): CTBN

2.1.1.2 Chemical modification

Modification of the chemical structure of the resin monomers can be used to reduce the cross-link density of the cured polymer and hence increase toughness [2]. This may involve incorporation of epoxy or curing agent (usually amine) components either of lower functionality or with increased backbone flexibility. Such modifications nearly always lower the thermal performance of the cured resin, and are generally unsuitable for high performance applications.
Chapter 2: Hyperbranched polymers as resin modifiers

2.1.1.3 Addition of thermoplastic modifiers

Addition of between 10 and 30% of a suitable thermoplastic (for example a PES) is widely used in the toughening of thermosets [1, 2, 6]. Initially, a miscible blend is formed; the thermoplastic then precipitates during cure [1, 2, 6, 7]. This technique has been applied to a number of thermosets including epoxies, bismaleimides and cyanate esters. The advantage of this approach over other toughening methods is that the mechanical properties of the material are retained over a wider temperature range, thus making it more suitable for high performance resins [7]. The addition of a viscous thermoplastic modifier (generally a solid) to a low viscosity epoxy will increase blend viscosity and hence have implications for processability. Such toughened systems are too viscous to be employed in composite manufacturing processes other than pre-pregging [2].

2.1.2 Dendrimers and HBPs

Dendrimers and HBPs are globular and as such display considerably different material properties to their linear analogues [8-9]. In particular, viscosity is lower than that of linear polymers because of the reduced degree of chain entanglement possible for the globular polymers. Owing to this low viscosity, it was hoped that the addition of a dendrimer or HBP to a commercial resin system might result in a reduction in viscosity, combined with an enhancement of mechanical properties. The potential of these polymers as toughening agents has been identified [4, 10-12].

The ability to toughen whilst not impairing processability is not possessed by conventional toughening agents. A class of additives, the Boltorn polymers, was identified as potentially having this capability.

2.1.2.1 Boltorn E1

The Boltorn additives, developed by Perstorp Specialty Chemicals, have been shown to toughen certain difunctional, trifunctional and tetrafunctional epoxy resins [4, 10-13]. The additives consist of a highly branched polyester core, surrounded by aliphatic chains. These materials are available commercially in either epoxy or hydroxyl functionalised forms. Whilst the polymers are synthesised in a stepwise manner like dendrimers, they are not perfectly symmetrical and are, therefore,
This study has focused on the use of Boltorn E1, an epoxy functionalised additive. It was hoped that the presence of the epoxy groups would impart compatibility with the matrix resin to form an initially homogeneous blend. Its use as an additive to conventional structural resin systems has been evaluated. The resins investigated differ from those used in studies published by other groups. As the toughening of high functionality resins was reported [12], it was hoped that the Boltorn additives would toughen the high performance epoxy system TGDDM/DDS whilst enhancing its processability because of the low viscosity of the HBP.

Boltorn E1 is marketed as a toughening agent for epoxy/amine systems. The manufacturer claims that it will give dramatically improved fracture toughness, without affecting either processing viscosities or other mechanical or thermomechanical properties. They also claim that it imparts very good hot-wet performance and excellent chemical resistance to the resin system with which it is blended [15].

2.2 Results and discussion

2.2.1 Boltorn E1

2.2.1.1 Structure

Boltorn E1 has a tetrafunctional core, joined by ester linkages to branches consisting of three generations of dimethylolpropionic acid (2.2).

Surrounding this branched structure is a shell of unsaturated monofunctional carboxylic acids, joined to the core by ester linkages. The carboxylic acids are aliphatic, the suggested reagent given in the patent [14] being trans-9-octadecanoic acid (2.3).
Chapter 2: Hyperbranched polymers as resin modifiers

(2.2): First generation polyester

(2.3): trans-9-octadecanoic acid

The unsaturated acid moieties have been epoxidised using a peracetic acid; the resultant polymer has on average 11 reactive epoxy groups per molecule. $^{13}$C NMR spectroscopy of the material shows C=C groups to be present. The molar mass of Boltorn E1 is 10500 g.mole$^{-1}$, therefore of the 32 hydroxyl groups at the periphery of the third-generation core it can be calculated that on average 25 will be bonded by ester linkages to trans-9-octadecanoic acid and that 11 of these aliphatic chains are epoxy functionalised.

It can be inferred from the structure of trans-9-octadecanoic acid that the epoxy groups will be located within the aliphatic shell of Boltorn E1 and not at its surface. However, it is possible that the aliphatic chains could bend back on themselves, the two sections of the chain associating through non-polar interactions, leaving the
polar epoxy group towards the periphery of the molecule. This is especially likely to be true in solution with a polar solvent.

Boltorn E1 has a viscosity of 15000 mPa.s at 23 °C; its structure, as predicted by molecular modelling [16], is shown in figure 2.1. From the density and molar mass of Boltorn E1, the average size of a molecule may be calculated to be 3.2 nm; this correlates well with the size predicted by molecular modelling (figure 2.1).

![Figure 2.1: Structure of Boltorn E1](image)

**2.2.1.2 Characterisation**

Thermal analysis of Boltorn E1 has been carried out. DSC revealed an exotherm at 250 °C (figure 2.2), due to the opening of the reactive epoxy groups and cross-linking of the material. This cross-linking was also observed in the viscosity-
temperature profile, in which Boltorn E1 was observed to gel at 210 °C. DSC of the cured material reveals a $T_g$ of -45 °C. The cured material was very soft and rubbery at room temperature, with a modulus of the order of $10^4$ Pa. TG analysis showed the onset of decomposition to be 368 °C.

![DSC thermogram of Boltorn E1](image)

**Figure 2.2: DSC thermogram of Boltorn E1**

The recommended concentration of Boltorn E1 in a resin blend is 5 to 10 parts per hundred resin by mass (phr). In this study, Boltorn E1 was blended with various resin systems at 5, 10 and 20 phr. The thermal, mechanical and rheological properties of the blends have been studied and compared to those of the unmodified resins.

2.2.2 TGDDM/DDS

2.2.2.1 Blending

TGDDM (2.4) is a tetrafunctional epoxy resin commonly used in high-performance aerospace applications [2]. It is a high viscosity resin (12000 mPa.s at 50 °C) and is used here with the amine hardener DDS (2.5), which is a solid at room temperature. Therefore, TGDDM/DDS is a very high viscosity system.
Boltorn E1 was pre-mixed with the epoxy and then DDS added at 55 % of the stoichiometric amount assuming the reaction of both primary and secondary amines. If Boltorn E1 is blended with the resin at ambient temperature macroscopic phase separation of the additive from the resin occurs during cure. IR spectroscopy of the sticky layer from the surface of the material confirmed that it was largely Boltorn E1; the additive phase separates and migrates to the surface during cure. If Boltorn E1 is blended with the resin at elevated temperature (after pre-warming to 70 °C) this macroscopic phase separation does not occur.

$\text{(2.4): TGDDM}$

$\text{(2.5): DDS}$

2.2.2.2 Dynamic mechanical thermal analysis (DMTA)

DMTA suggested that the $T_g$ of TGDDM/DDS was not significantly affected by the presence of the Boltorn E1 (table 2.1).

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>259</td>
</tr>
<tr>
<td>5</td>
<td>256</td>
</tr>
<tr>
<td>10</td>
<td>255</td>
</tr>
<tr>
<td>20</td>
<td>256</td>
</tr>
</tbody>
</table>

Table 2.1: Effect of concentration of Boltorn E1 on the $T_g$ of TGDDM/DDS
Low temperature DMTA of the blends revealed a peak in tan $\delta$ at -35 °C corresponding to the glass transition of Boltorn E1. The increase in temperature compared to the $T_g$ of polymerised Boltorn E1 (which is -45 °C) is likely to be due to the interaction of the resin and additive. A degree of phase mixing would account for the slight increase in the $T_g$ of the Boltorn E1 phase and the slight reduction in $T_g$ of the TGDDM/DDS phase. However, the presence of two peaks in tan $\delta$ suggested that the blend was predominately two-phase. The $\beta$ transition for the resin was observed as a shoulder to the lower peak in tan $\delta$ at around -65 °C (figure 2.2).

![Figure 2.2: DMTA thermogram of TGDDM/DDS with 5 phr Boltorn E1](image)

The $T_g$ of a fully miscible blend can theoretically be calculated using the Fox equation [4]:

$$\frac{1}{T_g} = \frac{m_1}{T_{g1}} + \frac{m_2}{T_{g2}}$$

Where $m$ is the mass fraction and 1 and 2 denote the two components present (in this case TGDDM/DDS and Boltorn E1). Therefore, using the $T_g$s of the resin and Boltorn E1, a plot of the theoretical $T_g$ of the blend versus mass fraction of Boltorn E1 added can be constructed. If the experimental data fit the theoretical line then it may be inferred that a miscible blend has been formed.
In this case, the experimental data deviated significantly from the theoretical line, suggesting that the blend is immiscible (figure 2.3). The presence of two peaks in tan δ observed in the DMTA thermogram (figure 2.2) also suggested that the blend was immiscible.

![Figure 2.3: Fox equation analysis of TGDDM/DDS blends with Boltorn E1](image)

**Figure 2.3: Fox equation analysis of TGDDM/DDS blends with Boltorn E1**

### 2.2.2.3 TG analysis

TGDDM/DDS exhibited a two-stage thermal degradation (figure 2.4). TG analysis of the system showed that the first onset of degradation was essentially unaffected by the concentration of Boltorn E1 (table 2.2). However, the second onset of degradation was affected by the concentration of Boltorn E1 added (figure 2.4) but did not appear to vary in any logical way.

The initial onset of degradation for TGDDM/DDS was at a lower temperature than that of Boltorn E1. The blends began to degrade at approximately the same temperature as TGDDM/DDS and also exhibited a two-stage decomposition (figure 2.4). This may be due to the high aromatic, thermally stable, content of TGDDM/DDS. The first decomposition stage may be due to the aliphatic content and the second stage the aromatic components.
Figure 2.4: TG analysis of TGDDM/DDS blends with Boltorn E1

Table 2.2: Effect of concentration of Boltorn E1 on the onset of degradation of TGDDM/DDS

2.2.2.4 Rheology

The viscosity of the system, when cured at 180 °C, was essentially unaffected by the presence of the additive (figure 2.5). The gel time was taken as the time at which the storage and loss moduli cross and was not significantly affected by the concentration of Boltorn E1 present.
2.2.2.5 Morphology

TGDDM/DDS is transparent, whereas blends with Boltorn E1 were opaque. This suggested the presence of two phases. SEM of the blends was carried out in order to elucidate their morphology. This showed that Boltorn E1 aggregated within the resin to form spherical inclusions whose diameter increased with increasing concentration of the additive (figure 2.6). At a concentration of 5 phr of Boltorn E1 the average diameter of the inclusions was 1.5 μm, at 10 phr 2 μm and at 20 phr 3 μm. This morphology is equivalent to that displayed by conventional rubber toughening agents such as CTBN [3]. This two-phase morphology concurs with the immiscibility predicted by the Fox equation.
Fracture toughness testing of blends of TGDDM/DDS with Boltorn E1 was carried out. The stress intensity factor, $K_{IC}$, for the initiation of crack growth was determined using compact tension specimens. The results showed that Boltorn E1 did not have a toughening effect on the resin (figure 2.7). This is unsurprising when considered in conjunction with the morphology of the blends. Boltorn E1 formed a micron-scale secondary phase within the resin; commonly, a co-continuous morphology is required in order to toughen TGDDM/DDS [1, 2, 6]. In addition, Boltorn E1 forms a cross-linked elastomer on curing. As discussed in section 1.1 such additives generally have no toughening effect on highly cross-linked resin systems such as TGDDM/DDS, in which thermoplastic toughening agents are required owing to their greater ability to dissipate fracture energy.
2.2.3 XLVR16-2

The toughening of a trifunctional epoxy resin by the addition of a Boltorn additive has been reported [11]. As toughening TGDDM/DDS by the addition of Boltorn E1 proved unsuccessful, the effects of the additive on two resins with lower functionality were assessed. The resins investigated were XLVR16-2 and XLVR15-2 (see section 2.4), supplied by the Advanced Composites Group (ACG). Boltorn E1 did not significantly enhance the processability of TGDDM/DDS (section 2.2.4). The ACG resins are of low viscosity and as such it is not expected that Boltorn E1 will enhance their processability. However, it was hoped that the additive would increase the toughness of the resins without having a negative effect on their processability.

XLVR16-2 consists of the trifunctional epoxy resin triglycidyl-p-aminophenol (TGPAP) (2.6) and the hardener 1-methyl-5-norbornene-2,3-dicarboxylic anhydride (2.7), in combination with an imidazole accelerator. The mixed resin has a viscosity of 200 to 300 mPa.s at 30 °C and is suitable for RTM and VARTM. Boltorn E1 has been blended with this resin as it displays good high temperature performance in combination with low viscosity.

Figure 2.7: Fracture toughness of TGDDM/DDS with increasing concentration of Boltorn E1.
Chapter 2: Hyperbranched polymers as resin modifiers

(2.6): TGPAP

(2.7): Methyl-5-norbornene-2,3-dicarboxylic anhydride

The curing agent contains a substituted imidazole blend at a concentration of 0 to 5 %, the remaining 95 to 100 % being 1-methyl-5-norbornene-2,3-dicarboxylic anhydride. The composition of the blend is a trade secret and has not been revealed by the resin manufacturer (ACG). It is known that 2-ethyl-4-methylimidazole (2.8) is commonly employed as an accelerator in anhydride cured systems [17, 18].

(2.8): 2-Ethyl-4-methylimidazole

The reaction between an epoxy and an anhydride may be accelerated by the addition of a nucleophile (often an imidazole). The lone pair of the imidazole nitrogen is able to donate electron density to the least sterically hindered carbon of
the epoxy ring. This weakens the carbon-oxygen bond which then opens (by an \( S_n2 \) type reaction), releasing the strain of the three-membered epoxy ring (figure 2.8) and resulting in the formation of a \( \beta \)-substituted alcohol.

![Figure 2.8: Formation of a \( \beta \)-substituted alcohol by nucleophilic epoxy ring opening (the nucleophile is represented by \( Y \)](image)

The alcohol group of the opened epoxy is then able to open the anhydride ring and accelerate the reaction between the epoxy and anhydride. The imidazolium ion formed by the donation of the imidazole lone pair to the epoxy carbon is stabilised by resonance in the ring (figure 2.9).

![Figure 2.9: Resonance in the imidazolium ring (the opened epoxy group is represented by \( R' \)](image)
The reaction between an epoxy and an anhydride is complex and involves several competing steps [19]. The most important of these are shown in figures 2.10 to 2.12.

**Figure 2.10:** Opening of anhydride ring with a hydroxyl group to form a monoester

**Figure 2.11:** The carboxylic acid group of the opened anhydride reacts with an epoxy group to yield an ester linkage
2.2.3.1 DMTA and DSC

The $T_g$ of the blends decreased slightly with increasing concentration of Boltorn E1 (table 2.3). Low temperature DMTA did not resolve a low temperature peak in tan $\delta$ corresponding to the glass transition of Boltorn E1. This single peak in tan $\delta$ could suggest single-phase morphology.
Chapter 2: Hyperbranched polymers as resin modifiers

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DSC</td>
</tr>
<tr>
<td>0</td>
<td>189</td>
</tr>
<tr>
<td>5</td>
<td>189</td>
</tr>
<tr>
<td>10</td>
<td>184</td>
</tr>
<tr>
<td>20</td>
<td>182</td>
</tr>
</tbody>
</table>

Table 2.3: Effect of concentration of Boltorn E1 on the T<sub>g</sub> of XLVR16-2

The Fox equation has been applied to the DMTA data (figure 2.13). The experimental data can be seen to deviate from the theoretical line, suggesting the two-phases are not fully miscible. However, the deviation is not as great as in the case of TGDDM/DDS, so there may be a stronger interaction between the phases in the case of XLVR16-2. The absence of a peak in tan δ corresponding to the glass transition of Boltorn E1 also suggested a stronger interaction between the phases than in the case of TGDDM/DDS.

Figure 2.13: Fox equation analysis of XLVR16-2 and Boltorn E1 blends
2.2.3.2 Rheology

The cure profiles of the blends at 60 °C suggest that neither viscosity nor gel time was significantly affected by the addition of Boltorn E1 (figure 2.14). The viscosity of the blends with 10 and 20 phr Boltorn E1 was higher than for 0 and 5 phr Boltorn E1 but this increase was not great enough to render the blends too viscous for RTM. Therefore, the addition of Boltorn E1 would not impair the suitability of this resin for resin infusion techniques. This increase in viscosity can be explained by the viscosity of Boltorn E1 (15000 mPa.s at 23 °C) being significantly higher than that of XLVR16-2 (200 to 300 mPa.s at 30 °C).

![Viscosity during cure of XLVR16-2 blended with Boltorn E1](image)

**Figure 2.14: Viscosity during cure of XLVR16-2 blended with Boltorn E1**

2.2.3.3 Morphology

SEM of blends of Boltorn E1 with XLVR16-2 has been carried out; it elucidated a two-phase morphology. Boltorn E1 agglomerated to form roughly spherical inclusions within the resin matrix (figure 2.15), which increased in size with increasing concentration of Boltorn E1. These inclusions of Boltorn E1 were on average 3 μm in diameter. This observation concurred with the phase separation suggested by the Fox equation. However, a smaller degree of immiscibility was observed than in the case of TGDDM/DDS (figure 2.6); this phase separation in XLVR16-2 was not sufficient for a peak in tan δ owing to Boltorn E1 to be resolved in the DMTA thermogram.
From the density and molar mass of Boltorn E1 the average size of a molecule may be calculated to be 3.2 nm diameter. The dimensions of the Boltorn E1 aggregates in the resin blends were larger than this by three orders of magnitude. It is not known whether this agglomeration was caused by physical interaction of the polymer molecules or by chemical bonding between them. The physical interactions may be chain entanglement, van der Waals forces, hydrophobic-hydrophobic interactions between the aliphatic chains of the shell or hydrogen bonding involving the polar hydroxyl and ester groups. Chemical bonding is possible in the form of cross-linking of the epoxy groups; the high temperatures used to cure the resins would favour epoxy opening and cross-linking. It has been shown (section 2.1.2) that Boltorn E1 will undergo homopolymerisation at elevated temperatures.

Figure 2.15: Scanning electron micrograph of XLVR16-2 with 20phr Boltorn E1

2.2.3.4 Fracture toughness

The effect of Boltorn E1 on the toughness XLVR16-2 was investigated. The fracture toughness of compact tension specimens of resins blended with 10 phr Boltorn E1 was compared to the unmodified resin (figure 2.16). The inclusion of Boltorn E1 at
this concentration had no significant effect on the toughness, measured as critical stress intensity factor ($K_{ic}$), of the resin.

The morphology of the resin blends has been shown by SEM to be broadly that of a rubber-toughened system, i.e. the additive formed micron-scale inclusions within the matrix resin. It was demonstrated that such an additive does not have a toughening effect on the highly cross-linked tetrafunctional epoxy resin system TGDDM/DDS. TGDDM is a tetrafunctional epoxy resin and as such has the potential to form a very highly cross-linked material. Despite the trifunctional nature of TGPAP it is unlikely that the cross-link density of XLVR16-2 will be significantly lower than that of TGDDM/DDS. This is due to both steric considerations (the tetrafunctional system is more constrained than the trifunctional one therefore not every epoxy ring is able to open and cross-link) and to the potential for intramolecular cyclisation of TGDDM. This high cross-link density makes these trifunctional and tetrafunctional resins very brittle.

![Figure 2.16: Fracture toughness of XLVR16-2 blended with Boltorn E1](image)

**Figure 2.16:** Fracture toughness of XLVR16-2 blended with Boltorn E1

### 2.2.4 XLVR15-2

XLVR15-2 is a low viscosity resin system supplied by ACG. The resin consists of 50 % TGPAP (2.6) and 50 % $N,N,N',N'$-tetraglycidyl-3,3'-diethyl-4,4'-
diaminodiphenylmethane (2.9), a tetrafunctional epoxy resin differing from TGDDM only by the presence of an ethyl group on each aromatic ring. The curing agent is 1-methyl-5-norbornene-2,3-dicarboxylic anhydride (2.7), of which 0 to 5 % is a substituted imidazole blend. The mixed resin and curing agent have a viscosity of 500 to 700 mPa.s at 30 °C. The resin is designed for use in VARTM.

(2.9): \(N,N,N',N'-\text{Tetraglycidyl-3,3'-diethyl-4,4'-diaminodiphenylmethane}\)

2.2.4.1 DMTA and DSC

The \(T_g\) of the system decreased slightly with increasing additive concentration (table 2.4). This decrease was smaller than that observed in the case of XLVR16-2. Low temperature DMTA did not clearly resolve a peak in tan \(\delta\) corresponding to the \(T_g\) of Boltorn E1. This suggested complete phase separation might not have occurred.

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
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<td>DSC</td>
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<td>10</td>
<td>216</td>
</tr>
<tr>
<td>20</td>
<td>215</td>
</tr>
</tbody>
</table>

| Table 2.4: Effect of concentration of Boltorn E1 on the \(T_g\) of ACG XLVR15-2 |

The Fox equation has been applied to the DMTA data (figure 2.17). The experimental data can be seen to deviate from the theoretical line, suggesting the
two-phases are not fully miscible. The deviation was similar to that observed for XLVR16-2.

**Figure 2.17:** Fox equation analysis of XLVR15-2

### 2.2.4.2 Rheology

**Figure 2.18:** Viscosity during cure of XLVR15-2 blended with Boltorn E1
The rheology profiles of the blends during cure at 60 °C showed that the additive did not significantly affect viscosity (figure 2.18). Boltorn E1 (15000 mPa.s at 23 °C) is of higher viscosity than XLVR15-2 (500 to 700 mPa.s at 30 °C) but addition of Boltorn E1 to the blend caused only a slight viscosity increase (figure 2.18) and did not render the resin unsuitable for resin infusion techniques.

2.2.4.3 Morphology

SEM of blends containing 10 and 20 phr Boltorn E1 are shown in figures 2.19 and 2.20. Although evidence of a two-phase morphology can be detected, large areas of the fracture surfaces examined appeared to be single phase. The secondary phase domains were of the order of 1 μm diameter for all concentrations of Boltorn E1. The fraction of secondary phase observed by SEM was less than would be expected for complete phase separation. The phase boundaries were less clearly defined than for XLVR16-2 and TGDDM/DDS, less contrast between the phases was observed by SEM. This suggested that XLVR15-2 and Boltorn E1 displayed a degree of miscibility.

Figure 2.19: Scanning electron micrograph of XLVR15-2 with 10 phr Boltorn E1
2.2.4.4 Fracture toughness

Boltorn E1 was shown to have no significant effect on the fracture toughness of XLVR15-2 when added at a concentration of 10 phr (figure 2.21). XLVR15-2 may be expected to have a similar cross-link density to TGDDM/DDS and XLVR16-2 and so this result is not surprising. However, in the case of XLVR15-2, Boltorn E1 did not clearly display the morphology of a rubber toughening agent. It appeared to be partially miscible with the resin matrix, causing a slight degree of plasticisation (table 2.4).

Batch variability in the glass transition of XLVR15-2 has been observed (figure 2.22). The lower temperature peak in tan δ of batch 1, as observed by DMTA, can be seen as a shoulder to the peak in tan δ for batch 2. The corresponding higher Tg peak is barely discernible as a shoulder to the batch 1 peak in tan δ. This suggests that the two epoxy resin components present, TGPAP (2.6) and ethyl-modified TGDDM (2.9), may have been mixed in different proportions in the two batches.
Therefore, the use of XLVR15-2 as a matrix resin will not be further investigated. This batch variability has been shown to affect the thermal properties of the resin (figure 2.22) and so will prevent comparison of specimens made from different batches. An additive might be shown to enhance the properties of one batch of the resin but not to have the same effect on another batch. Therefore, this resin would not be suitable for use in the manufacture of structural components.
2.2.5 DGEBA/piperidine

It has been shown that Boltorn E1 does not toughen the highly cross-linked epoxy resin systems TGDDM/DDS, XLVR15-2 and XLVR16-2. Therefore, the addition of Boltorn E1 to a lower functionality epoxy resin has been investigated. These difunctional systems have a lower $T_g$ than the resins studied so far but are commonly used in composite and adhesive applications. Difunctional epoxy resins are effectively toughened by rubbers such as CTBN (2.1) \[3, 20\]. Owing to its rubbery nature, Boltorn E1 also has the potential to toughen these resins \[4, 21\].

The effects of the addition of Boltorn E1 to an epoxy resin system comprising DGEBA (2.10) and the cross-linking agent piperidine (2.11) were evaluated. Piperidine was added to the resin at a concentration of 5 phr. The secondary amine can open an epoxy ring; the tertiary amine formed by this reaction is able to act as a catalytic cross-linking agent by opening further epoxy rings using its nitrogen lone pair. The opened epoxide group is able to react with further rings (figure 2.23).

\[
\text{(2.10): DGEBA}
\]

\[
\text{(2.11): Piperidine}
\]

*Figure 2.23: An opened epoxide group reacts with a closed epoxy ring to yield an ether*
Boltorn E1 was blended with DGEBA and piperidine at concentrations of 0, 5, 10 and 20 phr. The amount of piperidine added was increased with the concentration of Boltorn E1 added to maintain a constant epoxy:amine molar ratio.

2.2.5.1 DMTA

DMTA of the blends showed that increasing the concentration of Boltorn E1 caused a decrease in the $T_g$ of the resin (table 2.5, figure 2.24), suggesting it imparted a degree of plasticisation.

The $T_g$ of Boltorn E1 has been found to be -45 °C by DSC. Low temperature DMTA of the blends did not elucidate a peak corresponding to the glass transition of Boltorn E1, only one peak in tan δ was observed. This suggested that the blends will be miscible and hence single phase. The reduction in $T_g$ was greater for this system than that for the resins previously studied that displayed two-phase morphology. A single-phase morphology would imply strong interaction between the resin and Boltorn E1.

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>Mean $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>86</td>
</tr>
<tr>
<td>20</td>
<td>72</td>
</tr>
</tbody>
</table>

*Table 2.5: Effect of concentration of Boltorn E1 on $T_g$*

A β transition, corresponding to the motion of polymer chain segments, was visible at around -70 °C in the DMTA thermograms of the cured resins. The temperature at which the peak in tan δ corresponding to the β transition occurred did not show an obvious correlation with concentration of Boltorn E1 added (table 2.6).

The height of the peak in tan δ at the β transition decreased slightly with increasing concentration of Boltorn E1 (table 2.7). This slight reduction in the height of the tan δ peak might suggest that the resin segments that relaxed at this temperature became more constrained with increasing concentration of Boltorn E1.
Chapter 2: Hyperbranched polymers as resin modifiers

Figure 2.24: Effect of concentration of Boltorn E1 on tan δ for DGEBA/piperidine

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>Mean β transition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-69</td>
</tr>
<tr>
<td>5</td>
<td>-65</td>
</tr>
<tr>
<td>10</td>
<td>-70</td>
</tr>
<tr>
<td>20</td>
<td>-74</td>
</tr>
</tbody>
</table>

Table 2.6: Effect of concentration of Boltorn E1 on the position of the β transition of DGEBA/piperidine

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>Mean β transition (tan δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.061</td>
</tr>
<tr>
<td>5</td>
<td>0.059</td>
</tr>
<tr>
<td>10</td>
<td>0.049</td>
</tr>
<tr>
<td>20</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Table 2.7: Effect of concentration of Boltorn E1 on the height of the β transition of DGEBA/piperidine
Using the Fox equation, the theoretical and experimental $T_g$s of the blends have been plotted (figure 2.25). The experimental points correlated well with the theoretical line, suggesting that a fully miscible blend had been formed.

![Figure 2.25: Fox equation analysis for DGEBA/piperidine blended with Boltorn E1](image)

**2.2.5.2 TG analysis**

TG analysis of the cured blends showed that Boltorn E1 and DGEBA begin to degrade at similar temperatures. Degradation of Boltorn E1 began slightly before that of the epoxy resin and resulted in zero residual mass at 1000 °C, compared to 4.7 % residual mass for the resin (figure 2.26). The blends all had an onset temperature almost identical to that of the neat resin. The residual mass for the blends was higher than that of the neat resin. This suggested a strong interaction between the resin and additive, the residual mass at 5, 10 and 20 phr Boltorn E1 increasing with the added mass of additive (table 2.8) but not in direct proportion to it.
Figure 2.26: TG analysis of DGEBA/piperidine blends with Boltorn E1

<table>
<thead>
<tr>
<th>Mass % of Boltorn E1 (%)</th>
<th>Residual mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.7</td>
</tr>
<tr>
<td>4.5</td>
<td>5.9</td>
</tr>
<tr>
<td>8.7</td>
<td>6.7</td>
</tr>
<tr>
<td>16.0</td>
<td>7.3</td>
</tr>
<tr>
<td>100</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2.8: Residual mass of DGEBA/piperidine and Boltorn E1 blends

2.2.5.3 Rheology

The rheology of the blends was followed during cure at 120°C. Increasing the concentration of Boltorn E1 had no significant effect on the viscosity of the blends. The gel time of the blends showed some variation (table 2.9) but this did not show an obvious correlation to concentration of Boltorn E1. The variation may, in part, be due to inconsistency in the time taken to load the sample into the rheometer and equilibrate at 120 °C.
Table 2.9: Gel time of DGEBA/piperidine blended with Boltorn E1

2.2.5.4 Morphology

SEM of the resin blends revealed a homogeneous morphology; Boltorn E1 appeared to be miscible with the epoxy system (figure 2.27). Owing to the lack of phase separation it was unlikely that Boltorn E1 would toughen this material, as it has been reported that a two-phase morphology is required for it to be effective [4]. The blends of Boltorn E1 with DGEBA and piperidine were transparent; those with TGDDM/DDS, XLVR16-2 and XLVR15-2 were translucent (all the unmodified resins were transparent). These observations agree with the morphologies observed; a single-phase product would be transparent. Materials consisting of more than one phase would not be transparent unless the phases had the same refractive index or the phase dimensions were smaller than the wavelength of visible light.
2.2.5.5 Fracture toughness

Fracture toughness testing showed that Boltorn E1 was ineffective in toughening DGEBA/piperidine at the concentrations tested (figure 2.28).

Conventional rubber toughening agents require a two-phase morphology to be effective, so the lack of toughness enhancement in this case was unsurprising. Thus far, the behaviour of Boltorn E1 has conformed with that of rubber toughening agents; it has failed to toughen trifunctional and tetrafunctional epoxy resins and also a difunctional resin when present as a miscible blend. Therefore, it was decided to change the curing agent employed in order to yield a two-phase system and so investigate the effect of Boltorn E1 as a secondary phase within a difunctional epoxy resin.
2.2.6 DGEBA/Jeffamine D230

Jeffamine D230 (2.12) is an aliphatic amine curing agent commonly used with DGEBA (2.10) [3]. It was added to the epoxy at a concentration giving a 1:1 epoxy:amine ratio, assuming reaction of both the primary and secondary amine. Owing to the flexible, aliphatic backbone of Jeffamine D230, the thermal properties of the blend will be reduced with respect to the DGEBA/piperidine system. The addition of Boltorn E1 yields a two-phase morphology (section 2.6.4).

\[
\text{(2.12): Jeffamine D230}
\]
2.2.6.1 DMTA

DMTA of the blends showed that increasing the concentration of Boltorn E1 caused a slight decrease in the $T_g$ of the resin (table 2.10, figure 2.29). The $T_g$ of unmodified DGEBA/Jeffamine D230 is 84 °C, compared to 98 °C for DGEBA/piperidine (section 2.5.1). This lower value is due to the more flexible nature of Jeffamine D230 with respect to piperidine and the higher concentration in which it is added.

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>Mean $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>20</td>
<td>79</td>
</tr>
</tbody>
</table>

*Table 2.10: Effect of concentration of Boltorn E1 on $T_g$ of DGEBA/Jeffamine D230*

The decrease in $T_g$ on increasing concentration of Boltorn E1 was smaller than that observed in the case of DGEBA/piperidine. Therefore, a smaller degree of plasticisation was caused by the addition of Boltorn E1 to DGEBA/Jeffamine D230 than to DGEBA/piperidine. A plasticising effect implies interaction between the
phases, the presence of Boltorn E1 decreasing the cross-link density of the cured material. This suggested more phase separation had occurred in this case than for DGEBA/piperidine in the presence of Boltorn E1.

Low temperature DMTA revealed a small peak in tan δ at around -50 °C (table 2.11). This peak may correspond to the β transition for the resin but increased in size with concentration of Boltorn E1, suggesting that it represented the superpositioning of the β transition and glass transition of Boltorn E1. In the case of the single-phase DGEBA/piperidine blends the height of this low temperature peak decreased with increasing concentration of Boltorn E1, suggesting it corresponded to the β transition alone. The formation of a homogeneous blend results in only one T_g being resolved for the system. It can be inferred that the two peaks in tan δ observed for DGEBA/Jeffamine D230 correspond to the presence of two phases, one consisting mainly of Boltorn E1 and the other mainly of the epoxy resin.

<table>
<thead>
<tr>
<th>Concentration of Boltorn E1 (phr)</th>
<th>Peak tan δ (°C)</th>
<th>Height of peak tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-58</td>
<td>0.039</td>
</tr>
<tr>
<td>20</td>
<td>-49</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Table 2.11: Low temperature peak in tan δ from DMTA of DGEBA/Jeffamine D230

Fox equation analysis of the blends concurs with a two-phase morphology. The experimental data deviated significantly from the theoretical line for a miscible blend (figure 2.30).
2.2.6.2 TG analysis

TG analysis of the cured blends showed that DGEBA/Jeffamine D230 began to decompose at a lower temperature than Boltorn E1 did (figure 2.31). DGEBA/Jeffamine D230 exhibited a two-stage mass loss, whereas that of Boltorn E1 was single stage. The onset temperature of the first stage did not vary with concentration of additive but the residual mass after the first stage of the decomposition did, decreasing slightly with increasing concentration of Boltorn E1 (table 2.12). Boltorn E1 had 1% residual mass at 500 °C, whereas DGEBA/Jeffamine D230 retained approximately 20% of its mass at this temperature. Therefore, with increasing concentration of Boltorn E1 a higher proportion of the blend will have degraded at this point. This decrease was not directly proportional to the mass percent of Boltorn E1 added.
Figure 2.31: TG analysis of DGEBA/Jeﬀamine D230 blends with Boltorn E1

<table>
<thead>
<tr>
<th>Mass % of Boltorn E1 (%)</th>
<th>Residual mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>3.7</td>
<td>17</td>
</tr>
<tr>
<td>7.1</td>
<td>16</td>
</tr>
<tr>
<td>13.1</td>
<td>15</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2.12: Residual mass of DGEBA/Jeﬀamine D230 and Boltorn E1 blends at 500 °C

2.2.6.3 Rheology

The rheology of the blends was followed during cure at 100 °C (ﬁgure 2.32). Increasing the concentration of Boltorn E1 had no signiﬁcant effect on initial viscosity. The gel time of the blends varied by only a few seconds, so it may be concluded that the concentration of Boltorn E1 did not impair the processability of this resin.
2.2.6.4 Morphology

In contrast to the blends with piperidine, these materials displayed clear two-phase morphology (figure 2.33), suggesting Boltorn E1 had phase separated during cure from the initially homogeneous blend. This morphology agreed with the immiscibility of the two phases predicted by comparing the experimental $T_g$s to theoretical ones for a miscible blend predicted by the Fox equation.
2.2.6.5 Fracture toughness

Literature reports suggest that Boltorn E1 has the ability to toughen difunctional epoxy resins in which phase separation occurs [4]. Therefore, it was hoped that the additive would toughen DGEBA/Jeffamine D230. However, at a concentration of 10 phr no significant toughening effect was observed (figure 2.34).

Figure 2.33: Scanning electron micrograph of DGEBA/Jeffamine D230 with 10 phr Boltorn E1
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2.3 Conclusions

Boltorn E1 has been blended with various tetrafunctional, trifunctional and difunctional epoxy resins at concentrations of 5, 10 and 20 phr. The resin blends have been characterised in terms of some of their thermal, rheological and mechanical properties. It has been shown that, whilst having a negligible impact on processability, Boltorn E1 failed to increase the fracture toughness of the blends.

Boltorn E1 is less viscous than TGDDM/DDS and is of comparable viscosity to the DGEBA systems. It has been shown to have a negligible effect on the viscosity of these systems. Boltorn E1 is more viscous than XLVR16-2 and XLVR15-2 and as such has been shown to slightly increase the viscosity of these blends. These increases were not great, in part because of the low concentration of the additive (20 phr equates to 7.7 weight % in XLVR15-2 and 8.2 weight % in XLVR16-2). The processing window of the resins was not significantly affected by the addition of Boltorn E1.

The blends showed a correlation between morphology and degree of plasticisation. The highly phase-separated systems TGDDM/DDS and DGEBA/Jeffamine D230

Figure 2.34: Fracture toughness data for DGEBA/Jeffamine D230 blended with Boltorn E1
show the smallest depression of $T_g$ on addition of Boltorn E1; DMTA of these materials clearly revealed a glass transition for the Boltorn E1 phase. This was as would be expected for a phase-separated system, the $T_g$ of each phase was clearly resolved and was little changed from that of the pure material. XLVR16-2 and XLVR15-2 showed a higher degree of compatibility and, therefore, a greater depression in matrix resin $T_g$ on addition of Boltorn E1. Low temperature DMTA did not clearly resolve a glass transition corresponding to Boltorn E1. DGEBA/piperidine appeared to be fully miscible with Boltorn E1 at the concentrations examined. The decrease in matrix resin $T_g$ was greatest for this system and as the blend is single phase, no glass transition corresponding to Boltorn E1 was observed. The plasticisation observed in the blends was due to the high epoxy equivalent weight of Boltorn E1 with respect to the resins. This caused a reduction in the cross-link density of the resins.

The use of Boltorn additives as toughening agents for epoxy resins has been reported in the literature. Toughness enhancements have been reported for difunctional, trifunctional and tetrafunctional resins. The differences between the literature systems and those examined in this work are detailed below and assist in explaining the difference in the toughening behaviour achieved.

### 2.3.1 Difunctional resins

Ratna and Simon [10] have reported a significant increase in the impact strength of a DGEBA resin system on the addition of a Boltorn additive. The curing agent used is diethylenetriamine, employed in a stoichiometric quantity. In this case the Boltorn material consists of a core similar to that described in section 2.1.1 but consisting of 5 generations rather than 3. The material has no shell of aliphatic chains and so is hydroxyl functionalised. The material is unable to form chemical cross-links with itself and instead agglomerates by strong hydrogen bonding [10]. Therefore, this additive is a thermoplastic. It is not able to open the DGEBA epoxy groups at the cure temperature employed and so forms hydrogen bonds, not covalent cross-links as in Boltorn E1 [12], with the resin.

In order to increase impact strength significantly a high concentration of the additive must be used, for example 20 % by mass of the total blend to double the impact strength. This is a higher concentration than the 20 phr maximum added to
DGEBA/piperidine and DGEBA/Jeffamine D230. SEM of the blends [10] reveals a morphology approaching co-continuity for 20 weight % of the additive. Therefore, the hydroxyl functionalised Boltorn additive is behaving in a similar manner to a conventional thermoplastic toughening agent and as such may be expected to toughen high performance epoxy resins. It must also be noted that the mechanical property measured in this case is impact strength and not fracture toughness.

Mezzenga and Manson have reported an increase in $K_{ic}$ for a DGEBA resin on addition of Boltorn E1 [4]. An increase of approximately 50 % is observed on addition of 5 phr of the additive and nearly 100 % with 20 phr of Boltorn E1. The curing agent used is isophorone diamine. Boltorn E1 is able to form chemical cross-links with itself and with the matrix resin. It is reported to toughen by cavitation and plasticisation, i.e. by the same mechanism as conventional rubber toughening agents such as CTBN [3]. The degree of toughening in this system is slightly higher than that caused by CTBN. The major advantage of the use of Boltorn E1 is that, at a concentration of 20 phr, the initial viscosity of the blend is an order of magnitude lower than a blend with the same concentration of CTBN [4].

The curing agent used by Mezzenga and Manson is different to those used in this work. It is possible that changing the curing agent from piperidine or Jeffamine D230 to isophorone diamine would result in a toughening effect. The interaction between the additive and curing agent will affect the morphology of the blend and hence influence the toughness of the blends.

The values of $K_{ic}$ achieved for DGEBA/piperidine and DGEBA/Jeffamine D230 were approximately twice those reported in the literature for the unmodified difunctional resin [3, 4]. This may suggest that the crack generated in the compact tension specimens was not sufficiently sharp to give the minimum value of toughness, as required by the standard [22]. Repetition of the fracture toughness tests for these systems, ensuring a sharp, natural crack is generated, may yield different results.

### 2.3.2 Trifunctional resin

Ratna and Simon have blended the same hydroxyl-functionalised Boltorn additive with a trifunctional epoxy resin [11]. In this case, the epoxy is TGPAP and the curing agent, as in the difunctional system, is diethyltoluene diamine. The increase in
impact strength is less than for the difunctional blends, a 50% increase achieved with the addition of 20% Boltorn by mass. This smaller increase in impact strength is explained by the morphology of the blends. In this case, a single-phase morphology is observed, as in DGEBA/piperidine. Plasticisation of the matrix resin is observed, as the thermoplastic additive reduces its cross-link density. The additive does not form chemical bonds with the matrix [11] and so is able to toughen it by enhancing plastic deformation. In contrast, Boltorn E1 is able to form cross-links with the matrix resin through its epoxy groups and the degree of plasticisation possible is much lower. Therefore, the addition of Boltorn E1 to DGEBA/piperidine does not cause sufficient plasticisation to toughen the resin. The presence of Boltorn E1 causes a decrease in cross-link density as it has an epoxy equivalent weight of 875 g.mole\(^{-1}\) [15], compared to approximately 187 g.mole\(^{-1}\) for DGEBA. Therefore, a small degree of plasticisation is observed in the DGEBA/piperidine blends, which is not sufficient to toughen the resin.

### 2.3.3 Tetrafunctional resin

The toughening of TGDDM by the addition of Boltorn E1 has been reported [12]. The fracture toughness of carbon fibre composites of TGDDM with 15 phr of Boltorn E1 and a stoichiometric quantity of metaphenylene diamine was evaluated. An increase in \(G_{1c}\), the critical strain energy release rate, of 50% was achieved. This result suggests that a small degree of toughening is possible in a tetrafunctional epoxy by the addition of Boltorn E1. This result cannot be compared directly to the lack of toughening observed for TGDDM/DDS as there are too many differences between the two systems. These include the nature of the curing agent employed, the concentration of the additive, the presence of carbon fibres, the toughness parameter reported, the test method and the cure schedule. In addition, the resin that was toughened was a low viscosity version of TGDDM, suitable for RTM [12]. Therefore, it is likely that this resin contains low molecular weight species and reactive diluents and hence will interact differently with Boltorn E1 than the high viscosity TGDDM resin will.
2.3.4 Blend morphology

The epoxy functionality of Boltorn E1 allowed sufficient compatibility between the resin and additive that an initially homogeneous blend was formed with the resins investigated. The two-phase morphology revealed by SEM for the cured blends, except DGEBA/piperidine, was developed during the cross-linking process. Phase separation [23] occurs because of the decreasing solubility of the additive in the resin as polymerisation proceeds. Development of the secondary phase has been reported to be by a nucleation and growth process [21]. The secondary phase can grow until vitrification occurs, at which point a continuous network has been formed throughout the material and the morphology is frozen in.

In order to predict the morphology of a blend, the solubility parameters of the species present must be calculated [23-25]. All the initial blends were homogeneous, suggesting their solubility parameters were close in value. During the polymerisation process a large number of different oligomers are formed as the species present react and chain extension occurs. Therefore, predicting the solubility parameters of the species present in the reaction mixture is very complex and would require computer modelling. This analysis has not been carried out within this project.

The toughness of modified difunctional resins has been shown to depend on the morphology of the blend [21]. Phase separation of the additive from the resin is influenced largely by the chain end functionality of the additive. The morphology of the final product also depends on the processing conditions, i.e. on the composition of the blend and on the temperature at which the polymerisation reaction is carried out [25].

2.3.5 Toughening mechanisms

Boltorn E1 has been reported to toughen epoxy resins [3, 4] by particle cavitation and plastic deformation of the matrix. Cavitation occurs by void formation within the additive particles; plasticisation of the matrix resin takes place around phase boundaries, owing to mixing of matrix and additive at these points.
Cavitation occurs because of the higher coefficient of thermal expansion of the additive than the resin. Owing to this, on cooling after cure the additive will be under triaxial stress. When a crack splits a Boltorn E1 domain it can contract to yield a depression and negate this stress. This explains why SEM reveals the secondary phase as a series of depressions rather than a mixture of depressions and hillocks (figure 2.33) [3]. Fracture energy is employed in the creation of a void. Void formation reduces constraint in its vicinity and so facilitates plastic deformation.

Plasticisation aids in the dissipation of fracture energy as the stress yielding, and resultant plastic deformation, consume energy [4]. Highly cross-linked resins cannot be toughened by this method as the plastic deformation is largely constrained by the rigid matrix resin; therefore sufficient fracture energy cannot be dissipated in this manner to inhibit crack propagation.

Thermoplastics can successfully toughen highly cross-linked epoxy resins as they allow a greater degree of shear yielding than cross-linked elastomeric toughening agents do [1, 2]. Therefore, the use of a thermoplastic HBP or dendrimer may prove a more effective toughening agent to high performance resins than the thermoset Boltorn E1 does. A thermoplastic Boltorn additive has been shown to successfully toughen a trifunctional epoxy when present as a co-continuous phase. Therefore, an investigation into the use of thermoplastic dendrimers and HBPs would be worthwhile.

Dendrimers, although compact molecules owing to their ordered structure and globular nature, contain internal channels and voids [26]. These internal spaces may be instrumental in resin toughening by allowing plastic deformation within the molecule to a greater extent than a densely-packed structure would.

Linear thermoplastic toughening agents already exist [1, 2]; the potential advantage of dendrimers and HBPs over these agents is their lower viscosity. A Boltorn additive has been shown to decrease resin viscosity by an order of magnitude with respect to CTBN [4]. Therefore, thermoplastic dendrimers and HBPs have the potential to toughen highly cross-linked epoxy resins without increasing their viscosity. It would be interesting to evaluate the potential of hyperbranched analogues of conventional thermoplastic toughening agents, such as PES.
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2.4 Experimental

2.4.1 Instrumentation

IR spectra were recorded on a Perkin-Elmer Spectrum 2000 Fourier transform IR spectrometer. IR spectra were obtained in the absorption mode at a resolution of 1 cm\(^{-1}\) and 16 scans. Liquid samples were scanned on NaCl plates. \(^{13}\)C and \(^{1}\)H NMR spectra were obtained in the solution phase in CDCl\(_3\). \(^{13}\)C NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 100MHz and ambient temperature. \(^{1}\)H NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 400MHz and ambient temperature.

DSC was carried out under a nitrogen atmosphere using a TA Instruments 2920 Modulated Differential Scanning Calorimeter. Bending DMTA was performed using a Polymer Laboratories Mark II Dynamic Mechanical Thermal Analyser. DMTA was carried out on samples of average dimensions 25 x 10 x 2 mm\(^3\) in single cantilever mode, at a frequency of 1 Hz, strain x 4, and at a ramp rate of 2 K.min\(^{-1}\). Thermogravimetric analysis was performed in a nitrogen atmosphere using a Perkin-Elmer TGA7 Thermogravimetric Analyser, at a ramp rate of 10 K.min\(^{-1}\).

Rheology measurements were performed on a Rheometric Scientific ARES (Advanced Rheometric Expansion System) at 1 Hz between 25 mm diameter parallel plates and at temperatures in accordance with the cure cycle of the resin unless otherwise stated.

SEM of gold-coated fracture surfaces was carried out using a LEO 1550 Field Emission Scanning Electron Microscope.

Fracture toughness testing was carried out in accordance with ASTM D 5045-99, using compact tension specimens. Compact tension specimens (approximately 48 x 50 x 15 mm\(^3\)) were cast in a mild steel mould lined with Teflon release paper and degassed in a vacuum oven. The sawn-in crack and holes were machined. The natural crack was generated using a razor blade. Samples were tested on a Zwick 1484 machine with a 1 kN load cell unless otherwise stated, they were tested at room temperature (20 to 22 °C).

Elemental analyses were carried out on a Leeman Laboratories Inc CE440 Elemental Analyser.
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2.4.2 Materials

TGDDM and DDS were obtained from Vantico. The resins XLVR15-2 and XLVR16-2 were obtained from ACG. Boltorn E1 was obtained from Perstorp Specialty Chemicals of Sweden via ACG. DGEBA was obtained from Resolution Performance Products. Piperidine was obtained from Aldrich. Jeffamine D230 was obtained from Huntsman Performance Chemicals.

2.4.3 Boltorn E1

Boltorn E1 was cured in the ARES rheometer using a cone and plate (50mm diameter, cone angle 0.0198 radians). The material was heated from 25 °C to 300 °C at 2 K.min⁻¹ and 10 % strain. Modulated DSC was carried out on the uncured material (modulated at an amplitude of ±1 °C, 60 second period, underlying ramp rate 10 K.min⁻¹) and the cured material (modulated at an amplitude of ±1 °C, 60 second period, underlying ramp rate 3 K.min⁻¹). IR v_max: 3507, 2927, 2856, 1744, 1465, 1377, 1295, 1238, 1153, 1125, 1051, 1012, 723, 666, 652 cm⁻¹. Found: C, 66.63; H, 9.72 %. ¹H NMR (CDCl₃): (approximate relative intensities) δ = 0.9 (t, 3H, CH₃), 1.3 (m, 26H, CH₂), 2.3 (m, 10H, CH₂), 2.9 (s, 2H, CH₂), 3.5 (m, 5H, epoxy protons), 4.2 (m, 18H, CH₂ next to ester), 5.8 (d, trace, residual peracetic acid from epoxidation), 6.4 (d, trace, residual peracetic acid), 7.1 (m, trace, residual unepoxidised C=C). ¹³C NMR (CDCl₃): δ = 14.1, 17.3, 17.6, 17.7 (CH₃); 22.5, 24.8, 26.6, 27.8, 28.9, 29.0, 29.1, 29.2, 29.4, 29.5, 29.7, 31.6, 31.8, 34.0 (CH₂); 46.4, 46.5, 48.6 (CH₂ next to ester); 54.3, 57.2 (epoxy); 64.9 (CH₂ next to ester); 126.0, 128.9, 129.5, 129.8 (C=C); 171.7, 172.1, 173.1 (C=O).

2.4.4 TGDDM/DDS

TGDDM (50 g, 0.118 mol) and DDS (15.8 g, 0.0635 mol) were mixed with the appropriate concentration of Boltorn E1 (0, 2.5, 5 or 10 g; 0, 5, 10 or 20 phr) at 2400 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The mixture was then warmed in an oven at 70 °C for 5 minutes and remixed.
immediately on removal from the oven. It was cast on to a glass plate lined with Teflon release paper and degassed in a vacuum oven, then cured as a sheet approximately 2 mm thick between glass plates. The resin was cured for 6 hours at 180 °C and for 3 hours at 200 °C. DMTA was carried out on the cured blends; specimens were cut from the cured sheet and the edges polished. The blends were also cured in the rheometer at 5 % strain with a 10 g initial static force.

Compact tension specimens were cured for 20 hours at 95 °C, 3 hours at 120 °C, 2 hours at 150 °C, 2 hours at 180 °C and 4 hours at 200 °C. Specimens were tested with a crosshead displacement rate of 0.25 mm.min⁻¹.

2.4.5 XLVR16-2

Resin (20 g) and curing agent (25 g) were mixed at ambient temperature with the appropriate concentration of Boltorn E1 (0, 1, 2 or 4 g; 0, 5, 10 or 20 phr) at 2400 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The mixture was cast as a sheet approximately 2 mm thick between glass plates lined with Teflon release paper. It was cured for 24 hours at 60 °C, then heated at 20 K.hour⁻¹ to 175 °C and allowed to dwell at this temperature for 120 minutes. DMTA and DSC (modulated at an amplitude of ±1 °C, 60 second period, underlying ramp rate 3 K.min⁻¹) were carried out on the cured blends. DMTA specimens were cut from the cured sheet and the edges polished. The blends were also cured in the rheometer at 10 % strain.

Compact tension specimens were cured for 24 hours at 60 °C, then heated at 20 K.hour⁻¹ to 175 °C and allowed to dwell at this temperature for 120 minutes. Specimens were tested with a crosshead displacement rate of 0.25 mm.min⁻¹.

2.4.6 XLVR15-2

Resin (20 g) and curing agent (28.2 g) were mixed at ambient temperature with the appropriate concentration of Boltorn E1 (0, 1, 2 or 4 g; 0, 5, 10 or 20 phr) at 2400 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The mixture was cast as a sheet approximately 2 mm thick between glass plates lined with release paper. It was cured for 24 hours at 60 °C, then heated at 20
K.hour\(^{-1}\) to 200 °C and allowed to dwell at this temperature for 60 minutes. DSC (modulated at ±2 °C amplitude, 40 second period, underlying ramp rate 3 K.min\(^{-1}\)) and DMTA were carried out on the cured blends. DMTA specimens were cut from the cured sheet and the edges polished. The blends were also cured in the rheometer at 10 % strain.

Compact tension specimens were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 200 °C and allowed to dwell at this temperature for 60 minutes. Specimens were tested with a crosshead displacement rate of 0.25 mm.min\(^{-1}\).

2.4.7 DGEBA/piperidine

DGEBA (10 g) and Boltorn E1 (0, 0.5, 1 or 2 g, 0, 5, 10 or 20 phr) were mixed at 2400 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer and degassed in a vacuum desiccator. Piperidine (0.50, 0.50, 0.51 or 0.52 g, adjusted to maintain a constant epoxy:piperidine molar ratio) was added and the blend mixed gently with a spatula. The material was cast into a silicone rubber mould that had been sprayed with a silicone release agent. The specimens were cured for 16 hours at 120 °C. After cooling to ambient temperature the samples were demoulded. DMTA samples were polished to size. The blends were also cured in the rheometer using 50 mm parallel plates at 10 % strain.

Compact tension specimens were cured for 16 hours at 120 °C. Specimens were tested using an Instron 5500R tensometer with a 10 kN load cell and a crosshead displacement rate of 2 mm.min\(^{-1}\).

2.4.8 DGEBA/Jeffamine D230

DGEBA (20 g) and Jeffamine D230 (6.14, 6.22, 6.35 or 6.48 g) were mixed at ambient temperature with the appropriate concentration of Boltorn E1 (0, 1, 2 or 4 g, 0, 5, 10 or 20 phr). The blend was mixed at 2400 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer and then degassed in a vacuum desiccator. The material was cast into a silicone rubber mould that had been sprayed with a silicone release agent. The specimens were cured for 18 hours at 100 °C. After cooling to ambient temperature the samples were demoulded. DMTA
samples were polished to size. The blends were also cured in the rheometer between 50 mm parallel plates at 10 % strain.

Compact tension specimens were cured for 18 hours at 100 °C. Specimens were tested using an Instron 5500R tensometer with a 10 kN load cell and a crosshead displacement rate of 2 mm.min⁻¹.

### 2.5 References


[16] Model of Boltorn E1 by Dr David Porter, SMC, QinetiQ, August 2001


[22] Standard test methods for plane-strain fracture toughness and strain energy release rate of plastic materials, ASTM D 5045 - 99
Chapter 3: Conventional sol-gel hybrid synthesis
3.1 Introduction

3.1.1 Organic-inorganic hybrids

The concept of a material containing both organic and inorganic components has received much attention in the last ten years [1-14]. Organic-inorganic hybrid materials can offer dramatic improvements in mechanical, thermal and rheological properties over the purely organic polymers generally used in composite materials. The major property improvements that may be achieved using this approach have been demonstrated in numerous studies [1-14]. Improvements in properties such as strength, stiffness and high temperature/barrier performance, together with substantial reductions in flammability, moisture transmission and thermal expansion/contraction behaviour have been particularly noteworthy.

Organic-inorganic hybrid systems may exhibit the desirable properties of both the organic and inorganic phases [1, 2]. For example, an enhancement in mechanical properties offered by an organic phase could be combined with an enhancement in thermal properties offered by a stable inorganic phase. Therefore, the incorporation of inorganic material into an organic matrix resin could lead to the enhancement of these properties relative to the purely organic material. The successful development of such materials would contribute to the greater utilisation of composite, adhesive and other structural materials offering reductions in density and weight in comparison to conventional metallic materials.

Inclusion of the inorganic component on a nano-scale (i.e. with at least one phase dimension smaller than 100 nm) is important in many applications, as on this scale substantial property improvements over materials made by direct blending or inorganic-filler reinforcement are observed in some cases [15].

3.1.2 Hydrolytic sol-gel technique

This work makes use of the hydrolytic sol-gel approach to organic-inorganic hybrids. This technique involves the formation of an inorganic phase by hydrolysis and condensation of an inorganic precursor material, typically an alkoxyisilane [16]:

\[
\text{Hydrolysis: } \equiv \text{Si-OR} + \text{H}_2\text{O} \leftrightarrow \equiv \text{Si-OH} + \text{ROH} \quad (3.1)
\]
Alcohol condensation: \[ \equiv \text{Si-OR} + \text{HO-Si} = \rightarrow \equiv \text{Si-O-Si} = + \text{ROH} \] (3.2)

Water condensation: \[ \equiv \text{Si-OH} + \text{HO-Si} = \rightarrow \equiv \text{Si-O-Si} = + \text{H}_2\text{O} \] (3.3)

These inorganic oxide materials are ceramics; conventional ceramic processing involves high temperatures (typically greater than 1000 °C) [1, 17]. However, the sol-gel process, in which the inorganic phase is generated by the hydrolysis and condensation of an organometallic precursor solution, is carried out under comparatively mild conditions. Therefore, the sol-gel technique represents a facile, low-temperature route to the formation of inorganic oxides.

### 3.1.3 Hybrid synthesis

Most of the published literature in the field of sol-gel hybrids has focused on the formation of monolithic products or of thin films for coatings applications [18-21]. Owing to the exceptional properties of hybrids, in particular when nano-scale morphology is achieved, they have potential to be valuable additives to structural polymers. It is anticipated that the addition of these materials to conventional polymers, such as epoxy resin systems, could enhance both their mechanical and thermal properties. In order to be dispersible in a resin, and hence useful in such an application, the hybrid should have particulate morphology. Therefore, the aim of this work is the synthesis of organic-inorganic hybrid particles with phase dimensions smaller than 100 nm.

The organic HBP Boltorn E1, as described in Chapter 2, was chosen to be the organic component of the hybrids and silica, formed by the hydrolysis and condensation of an alkoxysilane, was chosen as the inorganic component. Boltorn E1 has a globular morphology and as such may favour a particulate morphology in the hybrid. It was hoped that the organic molecules would act as nucleation sites for the precipitation of silica. In this way, hybrid particles having an organic core and an inorganic shell can, in theory, be formed (figure 3.1). Formation of the hybrids as a very dilute dispersion should help to prevent interparticulate condensation by encouraging the growing particles to be physically separated.
3.2 Results and discussion

Silica hybrids of the HBP Boltern E1 have been synthesised by a hydrolytic sol-gel route. The alkoxysilanes used as the source of inorganic silica were TEOS (3.1) and TMOS (3.2). TEOS or TMOS were hydrolysed and condensed to form silica in the presence of Boltern E1. The hydrolysis of TMOS is considerably faster than that of TEOS [16]; its use is less common than that of TEOS because of the lack of control that is possible over its rapid kinetics and the toxic by-product of its hydrolysis, methanol (equation 3.2).

A solution of TEOS or TMOS was added to Boltern E1. The solvent employed, ethanol, acted as a co-solvent for the alkoxysilane, water, Boltern E1 and a catalyst. Water is produced by the condensation reaction (equation 3.3) and so theoretically two water molecules per alkoxysilane molecule is sufficient for complete hydrolysis.
However, hydrolysis does not go to completion even in the presence of excess water [16]. Therefore, water was added at a molar concentration of 15 times that of silicon (TEOS/TMOS plus 3-(triethoxysilyl)propyl isocyanate). The catalysts employed were acetic acid and hydrochloric acid. Condensation of the hydrolysed species leads to the formation of silica. The reaction was carried out in dilute solution to encourage the silica network to form around the polymer molecules and to discourage gelation (a continuous network forming throughout the solution).

### 3.2.1 Coupling agents

Boltorn E1 is soluble in TEOS. However, the organic and inorganic components of the hybrid, Boltorn E1 and silica, are inherently incompatible. This incompatibility was induced during the sol-gel reaction of TEOS. The hydrolysis and condensation of an alkoxysilane in the presence of Boltorn E1 led to a macroscopically phase separated product. A white solid (predominantly silica) in a pale yellow oil (predominantly Boltorn E1) was formed, as confirmed by IR spectroscopy.

Therefore, the use of a coupling agent, a molecule possessing both organic functionality and silane functionality, was investigated. The organic group was selected to react with Boltorn E1, yielding a polymer chemically modified with a small amount of silane. This enhanced the compatibility of the two phases by allowing covalent bonds to be formed between them. The silane groups grafted to Boltorn E1 were hydrolysed simultaneously with those of the added alkoxysilane in order to form a silica network that is bonded to Boltorn E1. In this way, the organic polymer can be covalently bonded to the silica network, forming a true copolymer.

#### 3.2.1.1 \( \text{Bis}[3-(\text{trimethoxysilyl})] \text{propyl amine} \)

The potential coupling agent initially investigated was a secondary amine, \( \text{bis}[3-(\text{trimethoxysilyl})] \text{propyl amine} \) (3.3).
Chapter 3: Conventional sol-gel hybrid synthesis

\((\text{MeO})_3\text{Si}^-\text{NH}\) \((\text{MeO})_3\text{Si}^-\)

**Figure 3.2:** Schematic representation of the reaction of \(\text{bis}[3-(\text{trimethoxysilyl})\text{propyl}]\text{amine}\) with Boltorn E1

(3.3): \(\text{Bis}[3-(\text{trimethoxysilyl})\text{propyl}]\text{amine}\)

The amine reacted with the dendritic polymer by opening its epoxy groups, resulting in the formation of a tertiary amine (figure 3.2). The tertiary amine formed by this reaction may then catalyse the opening of other epoxy groups and so has the potential to cause cross-linking of the dendrimer. Therefore, the amine has been added at a low concentration (equivalent to 20% of the concentration of epoxy groups) to minimise cross-linking. As there are eleven reactive epoxy groups per polymer molecule (see Chapter 2) this would give only 2.2 amine molecules per molecule of Boltorn E1 (molar mass 10500), and so impart only a slight degree of silane functionality.
The epoxy groups of Boltorn E1 are not situated on the periphery of the polymer but are within the shell of long aliphatic chains. Therefore, the aliphatic chains sterically hinder reaction of the epoxy groups with the amine. These chains are flexible and linear, and the structure of Boltorn E1 is rather open (figure 2.1), so this steric effect was not expected to inhibit the reaction. In a polar solvent the aliphatic chains may bend back on themselves to leave the epoxy ring at the periphery of the molecule and hence more readily available for reaction.

Boltorn E1 was dissolved in tetrahydrofuran to give a solution that is 50 % by mass HBP. Bis[3-(trimethoxysilyl)propyl]amine was added at a concentration of 2.2 moles per mole of Boltorn E1. Gelation occurred after the solution had been heated at 65 °C for 10 minutes. This was likely to be due to opening of the epoxy rings and cross-linking of the dendrimer, catalysed by the amine. It is not likely that formation of a silica network was the cause of gelation as the silane was present in a low concentration, only adventitious water present and no catalyst added. Heating the solution in the absence of the amine did not lead to gelation. Owing to the gelation observed, the use of this coupling agent was not further investigated.

3.2.1.2 3-(Triethoxysilyl)propyl isocyanate

The use of an isocyanate-functionalised coupling agent has been investigated. The free hydroxyl groups surrounding the core of Boltorn E1 can react with the isocyanate groups to form a urethane linkage (figure 3.3), this reaction being catalysed by a tertiary amine. The isocyanate used was 3-(triethoxysilyl)propyl isocyanate (3.4), and the catalyst 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (3.5).

(3.4): 3-(Triethoxysilyl)propyl isocyanate

(3.5): DBU
Chapter 3: Conventional sol-gel hybrid synthesis

Figure 3.3: Reaction of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate

This reaction was followed using IR spectroscopy to monitor the disappearance of the isocyanate absorption, which has a characteristic band at 2275 to 2250 cm\(^{-1}\) [22]. This is a strong absorption whose position is unaffected by conjugation. In this case the isocyanate absorption was observed at 2273 cm\(^{-1}\). The formation of the urethane may be followed by IR spectroscopy, a urethane linkage appearing at 1740 to 1690 cm\(^{-1}\) [22]. In this case the urethane linkage appeared at 1700 cm\(^{-1}\); it was not clearly seen as it overlapped the carbonyl absorption of Boltorn E1, which appears at 1744 cm\(^{-1}\) and so is observed as a shoulder to this stronger absorption.

Figure 3.4 shows the IR spectrum of Boltorn E1, in figure 3.5 3-(triethoxysilyl)propyl isocyanate and DBU have been added. The IR spectrum was taken whilst the reaction was incomplete; an absorption due to unreacted isocyanate is visible at 2273 cm\(^{-1}\) and the urethane linkage has appeared as a shoulder to the carbonyl absorption at 1700 cm\(^{-1}\).

Figure 3.4: IR spectrum of Boltorn E1
The Boltorn E1 molecules possess on average seven hydroxyl groups at the periphery of their core (Chapter 2, section 2.1.1). These groups are sequestered within the polymer by the aliphatic shell and are not easily available for reaction. However, IR spectroscopy showed that the reaction was successful, suggesting that the outer shell of Boltorn E1 is flexible and has an open structure. Owing to the success of this reaction, the use of 3-(triethoxysilyl)propyl isocyanate as a coupling agent was further investigated.

### 3.2.2 Drying Boltorn E1

The reaction of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate must be carried out in scrupulously dry conditions in order to prevent hydrolysis of the isocyanate or silane groups by any moisture present. The isocyanate can be hydrolysed to a carbamic acid, which then quickly loses CO₂ (which forms a carbonate ion) to yield a primary amine (figure 3.6).
Figure 3.6: Hydrolysis of 3-(triethoxysilyl)propyl isocyanate

3.2.2.1 Azeotropic distillation

A solution of Boltorn E1 in toluene was dried by azeotropic distillation prior to addition of 3-(triethoxysilyl)propyl isocyanate and DBU. If the solution was not dried prior to addition of the silane a gel was formed. When Boltorn E1 was heated alone it did not gel until a temperature of around 215 °C was reached. Therefore, it can be inferred that gelation of the modified Boltorn E1 was caused either by hydrolysis of the silane groups to form a silica network, or by cross-linking of the polymer molecules. The tertiary amine DBU has the potential to act as a catalyst for the opening and cross-linking of the epoxy rings.

DSC of Boltorn E1 revealed an exotherm at 250 °C, corresponding to the opening and cross-linking of the epoxy groups. Such an exotherm was not resolved in the DSC thermogram of Boltorn E1 blended with 0.5 mass % DBU (figure 3.7). A very small, broad exotherm was observed around 240 °C and the overall heat flow was increased with respect to Boltorn E1. This suggested that a single cross-linking event did not occur but that DBU may have catalysed curing, either it occurs throughout heating, resulting in the higher heat flow values, or that cross-linking occurred immediately on mixing, before the DSC experiment began.
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Figure 3.7: DSC thermogram of Boltorn E1 and Boltorn E1 with 0.5 mass % DBU

The reaction of Boltorn E1 (not dried) with 3-(triethoxysilyl)propyl isocyanate and DBU has been followed by IR spectroscopy. The epoxy bands of Boltorn E1 were observed at 1241, 876 and 799 cm⁻¹. These absorptions were present following gelation, suggesting that not all of the epoxy rings have been opened by the tertiary amine. The formation of a silica network was not evident in the IR spectrum. Si-O bands would appear at 1110 to 1000 cm⁻¹ and 900 to 600 cm⁻¹ [22] and are generally strong. This region of the spectrum of Boltorn E1 contains strong bands due to C-O stretching, O-H bending and C-H deformation, so it is possible that absorptions due to the presence of Si-O have been masked.

Drying Boltorn E1 by azeotropic distillation appears to have been successful. On addition of 3-(triethoxysilyl)propyl isocyanate and DBU gelation did not occur, unlike Boltorn E1 that has not been dried.

3.2.3 Modification of Boltorn E1

3-(Triethoxysilyl)propyl isocyanate was added to a dry solution of Boltorn E1 in toluene at a concentration of 10 moles per mole of the HBP. DBU was added as catalyst at 0.5 % by mass with respect to the total mass of reagents. After refluxing
for an hour approximately half the isocyanate had reacted with polymer (as observed by disappearance of the isocyanate absorption in the IR spectrum (figure 3.5)). The isocyanate absorption did not further reduce in size after heating at reflux overnight. Steric effects may have limited the extent of the reaction, as the hydroxyl groups with which the isocyanate reacts are not situated at the periphery of the polymer but are surrounded by the shell of long chain aliphatic carboxylic acid moieties. As the reaction proceeds steric crowding within Boltorn E1 will increase, making it progressively harder for the isocyanate molecules to reach the hydroxyl groups. In further work the concentration of 3-(triethoxysilyl)propyl isocyanate added was reduced to 7.5 moles per mole of Boltorn E1. As each Boltorn E1 has on average 7 hydroxyl groups per molecules, this gave a ratio of approximately one isocyanate molecule per hydroxyl group.

Reaction of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate must be carried out in a solvent that does not contain hydroxyl groups. 3-(Triethoxysilyl)propyl isocyanate can react with a hydroxyl group to form a carbamic acid, which then quickly loses CO₂ to yield a primary amine (figure 3.6). For example, in ethanol solution ethanolysis of the coupling agent took place rapidly. Complete loss of the isocyanate absorption in the IR spectrum was observed after 30 minutes at 50 °C. On addition of an alkoxysilane solution an opaque product was formed, suggesting a lack of compatibility between the organic and inorganic phases. Therefore, it can be inferred that reaction of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate had not occurred to a sufficient extent to compatibilise the two phases. Ethanol was present in far greater concentration than the HBP and also was more readily available for reaction with the isocyanate than the sequestered hydroxyl groups of Boltorn E1. Therefore, toluene, the solvent used for the azeotropic drying of Boltorn E1, was also employed as the solvent for the reaction with the coupling agent as it cannot hydrolyse or alcoholise the isocyanate groups.

### 3.2.4 Hybrid synthesis

Subsequent to modification of Boltorn E1 with isocyanate, toluene was removed from the reaction mixture under reduced pressure and the sol-gel reaction carried out in ethanol solution.
Hydrolysis of modified Boltorn E1 (now exhibiting some silane functionality) without addition of a further source of silica was attempted. It was not expected that the concentration of silane groups present would be sufficient to form a silica shell around the organic polymer molecules. The surface area of a Boltorn E1 molecule is approximately 32 nm²; fewer than seven silane groups would be attached to each HBP and this would be insufficient to form a silica network around the molecule. This hydrolysis reaction must be carried out in dilute solution in order to favour silica formation around individual polymer molecules and disfavour a macroscopic silica network forming throughout the solution.

Hydrolysis, induced by the addition of water and an acetic acid catalyst, yielded a pale yellow liquid after removal of solvent. The liquid nature of the product confirmed that the silane concentration was insufficient to form a silica network surrounding the polymer. If it had been a solid product would be formed, as the liquid organic polymer would be encapsulated in a solid silica shell. Therefore, an additional silane (TEOS or TMOS) was added to the modified Boltorn E1 in order to increase the concentration of silica in the product.

3.2.4.1 Addition of alkoxysilane

Both TEOS (3.1) and the more reactive TMOS (3.2) have been employed as the silica source for the sol-gel reaction. After removal of toluene from silane-modified Boltorn E1 an alkoxysilane solution was added. This solution consisted of TEOS or TMOS, water and an acid catalyst in ethanol. Both hydrochloric acid and acetic acid have been used as catalysts for this reaction. Ethanol was chosen as the solvent for the hydrolysis reaction as it acts as a co-solvent for water and TEOS/TMOS. The hybrid products were insoluble in ethanol due to their silica content and so precipitate out of solution as they form.

3.2.4.2 Concentration of the alkoxysilane

It was found that the minimum concentration of TEOS or TMOS that must be added to modified Boltorn E1 in order to form a solid product, suggesting complete encapsulation of the organic phase, was 75 moles per mole of polymer. When added in dilute concentration the reaction mixture did not gel, implying the formation of a hybrid sol.
In all cases (the use of TEOS and TMOS in combination with hydrochloric acid and acetic acid catalysts) the products formed on removal of ethanol and vacuum drying were pale yellow solids that were almost transparent (having the same degree of transparency as Boltorn E1). This implied that the organic and inorganic phases were associated on a nano-scale, as lack of compatibility at this level would give an opaque product due to the presence of phase boundaries. The products formed were monolithic and not particulate in nature; the sol particles had agglomerated on drying.

3.2.4.3 Nature of the catalyst

The use of hydrochloric acid as a catalyst for the hydrolysis yielded products that were slightly sticky. The pH of the alkoxysilane solution with hydrochloric acid was pH 2, which represents both the isoelectric point and the point of zero charge for the condensation of silica [16]. Therefore, the reaction would be at its slowest at this pH. The use of the acetic acid catalyst gave a pH of 4.5. The condensation of silica was more rapid in this case as the pH was not close to the isoelectric point. For the same reaction time the material synthesised with acetic acid will be more fully condensed and so will contain a greater proportion of solid silica than the hydrochloric acid catalysed material.

3.2.5 Characterisation

3.2.5.1 $^{29}$Si NMR spectroscopy

Formation of a silica network has been confirmed by solid state $^{29}$Si NMR spectroscopy of the hybrid materials. The degree of condensation of a silica network can be elucidated in this way, as peaks that are due to silicon attached to different numbers of O-Si groups occur at different chemical shifts. This is denoted, in the case that each silicon atom is bonded to 4 oxygen atoms, by $Q^n$ terminology [16], where n represents the number of bridging oxygen atoms (-OSi) bonded to the central silicon atom (n=0-4).

The $^{29}$Si NMR spectra showed a mixture of $Q^3$ and $Q^4$ species and a small $Q^2$ peak. The presence of the $Q^2$ and $Q^3$ peaks showed that silica condensation was not complete. This was expected because of steric constraints and the fact that
alkoxysilane hydrolysis was unlikely to have gone to completion [16]. The spectra also contained peaks corresponding to silicon bonded to three oxygen atoms and one carbon atom. These are known as T species and were due to the 3- (triethoxysilyl)propyl isocyanate moiety.

The use of TMOS and an acetic acid catalyst has been shown to increase the degree of silica condensation with respect to TEOS and hydrochloric acid (figures 3.8 and 3.9, table 3.1). This was due to the increased rate of hydrolysis of TMOS with respect to TEOS and the more effective nature of the acetic acid catalyst [16].

<table>
<thead>
<tr>
<th>Peak</th>
<th>TMOS, acetic acid</th>
<th>TEOS, hydrochloric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (ppm)</td>
<td>Proportion (%)</td>
</tr>
<tr>
<td>Q⁴</td>
<td>-110.1</td>
<td>53.7</td>
</tr>
<tr>
<td>Q³</td>
<td>-100.8</td>
<td>27.7</td>
</tr>
<tr>
<td>Q²</td>
<td>-91.3</td>
<td>5.0</td>
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<td>8.0</td>
</tr>
<tr>
<td>T¹</td>
<td>-46.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 3.1: $^{29}$Si NMR spectroscopy data on Boltorn E1 hybrids
Figure 3.8: $^{29}$Si NMR spectrum of hybrid sample synthesised using 75 moles TMOS per mole of Boltorn E1 and an acetic acid catalyst.

Figure 3.9: $^{29}$Si NMR spectrum of hybrid sample synthesised using 75 moles TEOS per mole of Boltorn E1 and a hydrochloric acid catalyst.
3.2.5.2 $^{13}$C NMR spectroscopy

$^{13}$C solid state NMR spectroscopy of the hybrid samples has been carried out (figure 3.10). All the peaks observed in the $^{13}$C NMR solution spectrum of Boltorn E1 were present, as were additional peaks attributable to the coupling agent. A small peak corresponding to an alkoxy carbon was also resolved. It is not possible to tell whether this peak was due to unreacted TEOS/TMOS, or to the alkoxy groups of the isocyanate coupling agent. The presence of this peak suggested that hydrolysis of the alkoxy groups had not gone to completion.

![13C NMR spectrum of hybrid sample synthesised using 75 moles TMOS per mole of Boltorn E1 and an acetic acid catalyst](image)

**Figure 3.10:** $^{13}$C NMR spectrum of hybrid sample synthesised using 75 moles TMOS per mole of Boltorn E1 and an acetic acid catalyst

3.2.5.3 DSC

DSC of the hybrid materials suggested that the thermal behaviour of the product depended on the catalyst used for silane hydrolysis. DSC of neat Boltorn E1 showed a $T_g$ at -53 °C and a cure exotherm at 258 °C, due to the opening and cross-linking of the epoxy groups.

DSC of hybrid materials synthesised with an acetic acid catalyst gave the same result for both TEOS and TMOS (figure 3.11). A $T_g$ was resolved at -40 °C and a cure exotherm was observed between 200 and 300 °C, due to the cross-linking of
Boltorn E1. This exotherm consisted of a peak with a shoulder at a higher temperature. The shoulder was probably due to the interaction of Boltorn E1 with the silica network, which may result in the organic component being constrained and hence a higher temperature required for cross-linking to take place. If a silica shell surrounded each Boltorn E1 molecule the exotherm due to cross-linking would not be seen as each organic molecule would be physically separated from the others.

For materials synthesised using a hydrochloric acid catalyst the cure exotherm was absent (figure 3.12). An endotherm was observed, centred at 64 °C in the case of TEOS and 347 °C for TMOS. The absence of the exotherm suggested that cross-linking of Boltorn E1 did not occur. It is possible that hydrochloric acid catalysed the ring opening of the Boltorn E1 epoxy groups. Therefore, cross-linking would have occurred prior to DSC being carried out and hence would not be seen in the thermogram. If this was the case the endotherm observed could be attributed to a melting transition of the partially cross-linked Boltorn E1 network. Cross-linking would not be expected to be complete, as Boltorn E1 would be physically constrained by the presence of silica. Alternatively, this endotherm, observed at around 70 °C in figures 3.11 and 3.12 could be due to the evaporation of the volatile molecules (water, ethanol and methanol) formed by the further condensation of alkoxy silane groups on heating. The absence of the exotherm could suggest that, in

Figure 3.11: DSC thermogram of Boltorn E1 hybrid synthesised with TEOS and acetic acid
this case, a molecular-scale hybrid had been formed. SEM and AFM were used to elucidate the morphology of the materials.

![DSC thermogram of Boltorn E1 hybrid synthesised using TEOS and hydrochloric acid](image)

**Figure 3.12: DSC thermogram of Boltorn E1 hybrid synthesised using TEOS and hydrochloric acid**

### 3.2.5.4 Effect of the catalyst on Boltorn E1

The effect of hydrochloric acid on Boltorn E1 is not clear from the IR spectra of the hybrid materials, the absence of the epoxy absorptions would indicate opening of the rings, but these bands are masked by the Si-O absorptions in the spectra of the hybrid materials.

Therefore, the effect of acetic acid and hydrochloric acid on a solution of Boltorn E1 in ethanol was investigated in the absence of silica. If hydrochloric acid catalyses ring opening sufficiently it may be expected that the solution would gel. This did not occur. The epoxy absorptions are not clear in the IR spectrum (figure 3.13), they would be expected at around 1250, 900 and 800 cm\(^{-1}\) [22].
Figure 3.13: IR spectrum of Boltorn E1 in ethanol solution with hydrochloric acid

The absence of cross-linking observed in the DSC thermograms could be explained by the morphology of the hydrochloric acid-catalysed hybrids. If the hybrid had formed on a molecular scale each organic molecule would be surrounded by a silica shell and so intermolecular cross-linking of the Boltorn E1 molecules would be prevented. In this case it is possible that at high temperature the intramolecular reaction of Boltorn E1 epoxy groups with hydroxyl groups at the periphery of its highly-branched core could have occurred.

3.2.5.5 TG analysis

TG analysis of the hybrid materials showed that those synthesised using TMOS began to degrade at the same temperature as for neat Boltorn E1 (368 °C) (figure 3.14). Those synthesised from TEOS began to degrade at a lower temperature. This decrease in mass was slow, the major mass loss occurring at approximately the same temperature as the TMOS hybrids and Boltorn E1. It is, therefore, likely that the slow mass loss was due to further silica condensation and loss of volatile condensation products (ethanol and water). The slower kinetics of TEOS hydrolysis means that, for the same reaction time, the TEOS hybrids will exhibit a lower degree of condensation than the TMOS hybrids [16]. Therefore, on heating further
hydrolysis and condensation of the TEOS hybrids occurred, leading to the formation of water and ethanol.

**Figure 3.14: TG analysis of Boltorn E1 and its silica hybrids**

The thermal stability of the silica present in the hybrids was higher than that of Boltorn E1. The residual mass of hybrid sample remaining after heating to 1000 °C was greater in the case of TMOS than TEOS. This may be due to the greater organic content of TEOS. Therefore, a greater percentage mass loss will be observed on heating TEOS than TMOS. However, the longer alkyl chain alone could not explain such a large difference in residual mass. Alternatively, the higher residual mass in the case of TMOS may be due to a greater degree of formation of stable silicon oxycarbide species [23, 24].

3.2.5.6 SEM

SEM of the hybrid materials (figure 3.15) suggested that the morphology was not affected by either the source of silica or the catalyst used for its hydrolysis. All the samples appeared platelet-like on a micron scale and two-phase on a nano scale. This suggested that the desired intimate association of Boltorn E1 with the silica network had been achieved.
Figure 3.15: Scanning electron micrographs of Bolton E1 hybrid synthesised with TMOS and acetic acid
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The micrographs (figure 3.15) showed the diameter of the clusters of Boltorn E1 to be of the order of 50 nm. This implied aggregation of the organic, as the diameter of a single Boltorn E1 molecule is calculated to be 3.2 nm. The aggregation of Boltorn E1 could be caused by DBU catalysing the cross-linking of the epoxy groups or by physical coalescence. Therefore, the organic and inorganic phases were not interlinked on a molecular level. However, the phase domains did appear to be nanoscale and as such may display the enhanced properties reported for such nanocomposites [3].

SEM did not resolve a significant difference between the hybrids synthesised using an acetic acid catalyst and those using a hydrochloric acid catalyst. A finer morphology could be implied in the case of the hydrochloric acid hybrids by the DSC thermograms (section 2.5.3); however, this was not resolved.

3.2.5.7 AFM

AFM of the hybrid samples was carried out in order to confirm the nano-scale morphology suggested by SEM. AFM was performed on samples catalysed with acetic acid (figure 3.16). Nano-scale structure was revealed; the samples appeared to consist of two phases, as revealed by both adhesion and topology studies. One phase consisting of globular domains of diameter less than 100 nm was clearly visible. Owing to the globular nature of Boltorn E1 it may be assumed that these domains were the organic phase. The second phase appeared to be continuous and so was assumed to be silica because of its ability to form an amorphous network.

The morphology of the sample synthesised using TEOS was less clear but appeared to have a finer morphology than that synthesised with TMOS, with phase dimensions significantly smaller than 100 nm. The rapid kinetics of TMOS hydrolysis may account for the larger phase domains, with hydrolysis and condensation occurring before as much phase mixing had occurred as in the case of TEOS.
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3.2.6 Concentration of alkoxy silane

TEOS/TMOS has been added at a concentration of 75 moles per mole of Boltorn E1, as this concentration was sufficient to give a solid product when used in conjunction with an acetic acid catalyst. The amount of TEOS/TMOS required to give a silica shell of a certain thickness may be calculated. It has been assumed that Boltorn E1 molecules are spherical and discrete. The diameter of a Boltorn E1 molecule may be calculated as 3.2 nm. In order to give a silica shell around each molecule of the same thickness as the radius of Boltorn E1, TEOS/TMOS would need to be added at a molar concentration of 2590 times that of the HBP.

Addition of TEOS/TMOS at a concentration of 75 moles per mole of Boltorn E1 would give an average silica shell thickness of 0.1 nm. This is less than the thickness of a silica monolayer (approximately 0.3 nm). However, it has been shown that aggregation of Boltorn E1 takes place. Association of the HBP may have
occurred either by physical coalescence or by chemical cross-linking. The opening and cross-linking of the epoxy rings could be auto-catalysed by the hydroxyl groups also present in Boltorn E1 or by the presence of DBU. Assuming Boltorn E1 formed aggregates that are on average 50 nm in diameter, the thickness of the silica shell, assuming spherical particles can be calculated as 5 nm.

The concentration of 75 moles of alkoxysilane per mole of HBP was chosen as it was the lowest to give solid products. Boltorn E1 agglomeration may have occurred because the amount of silica present in the hybrid was not sufficient to coat each molecule. Therefore, the concentration of alkoxysilane added was increased.

The concentration of TEOS/TMOS that must be added to give a silica shell of average thickness a quarter of the radius of a Boltorn E1 molecule (assuming spherical, discrete morphology) can be shown to be 353 moles of TEOS/TMOS per mole of Boltorn E1. Assuming the agglomeration of Boltorn E1 into 50 nm diameter aggregates this concentration would be expected to give a silica shell of average thickness 16 nm.

### 3.2.6.1 Synthesis with increased silica content

A hybrid material with TEOS added at a concentration of 353 moles per mole of Boltorn E1 was synthesised by the same method used for the materials with the lower alkoxysilane concentration. Gelation occurred 23 hours after addition of the alkoxysilane. The high concentration of TEOS facilitated the formation of a silica network; hence gelation occurred rather than the formation of a sol of discrete hybrid particles. The gel was opaque; this may be due to phase separation of Boltorn E1 from the silica gel or to the fact that the gelation occurred during mixing in an ultrasonic bath, leading to the formation of phase boundaries.

### 3.2.6.2 TG analysis

TG analysis showed the main onset of decomposition temperature for this material to be higher than for hybrids synthesised using the lower concentration of TEOS (377 °C, compared to 338 °C) (figure 3.17) because of the increased concentration of thermally stable silica. Therefore, it was assumed that the silica network was in some way constraining the organic material and inhibiting its decomposition. This suggested an intimate association of the two phases.
The hybrids showed a mass loss prior to the major decomposition event (figure 3.17), as also seen for the TEOS hybrids in figure 3.14. This may be due to the evaporation of water and ethanol from the sample, these volatile liquids being produced by further condensation to silica.

Figure 3.17: TG analysis of hybrid material synthesised with different TEOS concentrations

The higher concentration of TEOS, and hence silica, resulted in a higher residual mass after the decomposition of the organic material, as would be expected. TG analyses (figure 3.17) show the residual mass at 1000 °C to be 15 % for the lower TEOS concentration and 55 % for the higher concentration. Theoretical calculations show the percentage of silica in these samples to be 28 % and 64 % respectively. Therefore, in each case the residual mass was lower than predicted. This may have been due to the samples undergoing further condensation as they were heated, leading to a greater than theoretical mass loss. A mass loss due to further condensation was observed around 100 °C for the sample with the higher TEOS concentration and 200 °C for the lower TEOS concentration. This loss would lead to a smaller residual mass than would be calculated from the starting mass, as was observed experimentally.
3.2.6.3 DSC

DSC of the hybrid revealed a large endotherm centred at 82 °C (figure 3.18) that was much larger than that in the thermogram of the material synthesised using the lower concentration of TEOS (figure 3.11). This endotherm was most probably due to the evaporation of water and ethanol.

![DSC Thermogram](image)

**Figure 3.18: DSC thermogram of hybrid sample synthesised using 353 moles TEOS per mole of Boltorn E1**

This endotherm was larger for the material synthesised using a higher concentration of TEOS, as the concentration of water employed for the hydrolysis reaction was also increased correspondingly, i.e. water was added at a molar concentration 15 times that of TEOS plus 3-(triethoxysilyl)propyl isocyanate. This endotherm was a dominant feature of the DSC thermogram; it corresponds to the mass loss revealed by TG analysis (figure 3.17) at around 100 °C.

3.2.6.4 AFM

AFM of the hybrid samples has been carried out in order to elucidate their morphology. The material appeared to consist of two phases and to have nanoscale morphology, by both adhesion and topology studies (figure 3.19). However, the micrographs are not clear. This was due to experimental problems caused by the presence of an apparent fluid layer on the surface of the sample. This layer
caused very high adhesion between the tip and the sample, leading to the white band observed. This fluid layer may be water or ethanol, formed by further condensation of silica during analysis.

![Image of AFM images](image)

**Figure 3.19:** Pulsed force AFM – topographic (left) and adhesion (right) images of hybrid synthesised with 353 moles of TEOS per mole of Boltorn E1

### 3.3 Conclusions

Nano-scale hybrids of Boltorn E1 and silica have been successfully synthesised, as confirmed by microscopy studies. The domain sizes are of the order of 50 nm, showing that the organic and inorganic phases are not associated at a molecular level. It was hoped that an individual silica shell would coat each HBP molecule. However, a degree of aggregation of the organic phase has occurred.

The aim of the work was the synthesis of nano-scale hybrid particles. A particulate product was formed on condensation of silica but during the drying process these particles have agglomerated to form a monolithic product. This aggregation need not prevent evaluation of the hybrids as resin additives. These monoliths could be mechanically ground to a fine powder and then blended with an epoxy resin to determine their effect as a particulate dispersion.

The hybrids were formed from a dilute solution of Boltorn E1 in order to encourage the formation of a particulate product; these particles were observed to precipitate as silica condensation proceeded. Electron microscopy of the product prior to drying would give an indication of whether nano-scale particles had been formed. If this was found to be the case the use of alternative methods of product isolation, such
as centrifugation, filtration or freeze-drying could be investigated in order to preserve the particulate nature of the product. On removal of the solvent the product becomes more concentrated and so interparticular condensation is possible. Drying in this manner does not remove all the impurities present in the reaction mixture, for example products of the reaction of excess 3-(triethoxysilyl)propyl isocyanate with ethanol or water.

The aggregation of the organic phase by cross-linking of its epoxy groups could be catalysed by the presence of the tertiary amine, DBU. Alternatively, it could be autocatalysed by the hydroxyl groups present at the periphery of the core of Boltorn E1. Boltorn E1 was dried by azeotropic distillation. The high temperatures involved could favour homopolymerisation; therefore, an alternative, ambient temperature drying method, such as vacuum drying, may be preferable.

Both bis[3-(trimethoxysilyl)]propyl amine and DBU have the potential to catalyse the opening and cross-linking of the Boltorn E1 epoxy groups. The use of a coupling agent that is not able to do this may reduce the degree of agglomeration of Boltorn E1. Suggested reagents include GPTMS and (3-mercaptopropyl)trimethoxysilane. GPTMS could form hydrogen bonds with the HBP and also covalent bonds with unreacted hydroxyl groups at the periphery of the highly branched core of Boltorn E1. The mercaptan could react with the epoxy groups but, unlike an amine, would not catalyse cross-linking because of its less nucleophilic nature. The lone pairs of sulfur, unlike those of nitrogen, are shielded by d orbitals.

It was shown that the concentration of 75 TEOS/TMOS per HBP would not be sufficient to form a silica monolayer around each Boltorn E1 molecule, assuming spherical and discrete morphology. Therefore, the amount of alkoxysilane added was increased. A concentration of 353 TEOS per HBP caused the reaction mixture to gel. Dilution of the reaction mixture to increase interparticular distances or decreasing the concentration of TEOS could prevent gelation. AFM studies showed that the higher concentration of TEOS gave rise to a nano-scale hybrid. DSC and TGA showed that a high degree of further condensation occurred on heating the material, releasing volatile molecules. This would cause plasticisation if the hybrid had been blended with an epoxy resin and would be expected to significantly impair the thermal properties of the blend.
3.4 Experimental

3.4.1 Instrumentation

Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer. IR spectra were obtained in the absorption mode at a resolution of 1 cm\(^{-1}\) and 16 scans. Solid samples were scanned as KBr pellets, liquids and solutions were scanned on NaCl plates. Elemental analyses were carried out on a Leeman Laboratories Inc CE440 Elemental Analyser.

\(^{29}\)Si solid state direct polarised NMR spectroscopy was carried out on a Varian UNITYplus spectrometer against an external tetramethylsilane standard with magic angle spinning at a rate of 4100 to 4200 Hz. The spectra were obtained using a 90° pulse and a 30 second relaxation delay (1192 to 1872 repetitions). \(^{13}\)C NMR solid state spectra were obtained on an AC-300 Bruker spectrometer at a spin rate of 6.5 kHz with a relaxation delay of 1 second. Solution phase \(^{13}\)C and \(^{1}\)H NMR spectra were obtained in CDCl\(_3\). \(^{13}\)C NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 100 MHz and ambient temperature. \(^{1}\)H NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 400 MHz and ambient temperature.

DSC was carried out under a nitrogen atmosphere using a TA Instruments 2920 Modulated Differential Scanning Calorimeter, with modulation at an amplitude of ±1 K, a 60 second period and an underlying ramp rate 3 K.min\(^{-1}\). TG analysis was performed from 50 to 1000 °C under a nitrogen atmosphere using a Perkin-Elmer TGA7 Thermogravimetric Analyser, at a ramp rate of 10 K.min\(^{-1}\).

SEM of carbon-coated hybrids was carried out using a LEO 1550 Field Emission Scanning Electron Microscope. AFM was carried out (by David Grandy, IPTME, Loughborough University) using a Witec pulsed force module coupled to a TA Instruments 2990 Micro-Thermal Analyzer incorporating a TM Microscopes Explorer AFM. TM Microscopes integrated silicon probes were used, having a resonant frequency of 9-16 Hz, a force constant of 0.1 to 0.3 N.m\(^{-1}\) and a tip radius of approximately 10 nm.
3.4.2 Materials

Boltorn E1 was obtained from Perstorp Specialty Chemicals of Sweden via ACG. All other chemicals were obtained from Aldrich and were used as received.

3.4.3 Hybrid synthesis

3.4.3.1 Modification of Boltorn E1 with bis[3-(trimethoxysilyl)propyl]amine

Bis[3-(trimethoxysilyl)propyl]amine (0.625 g, 1.83 mmol) was added to a solution of Boltorn E1 (8 g, 0.762 mmol) in tetrahydrofuran (4.31 g) and the mixture stirred at 65 °C. After 10 minutes a pale yellow gel was formed.

3.4.3.2 Drying Boltorn E1 by azeotropic distillation

Boltorn E1 (2.5 g, 0.24 mmol) was dissolved in toluene (50 cm³) and the solution dried by azeotropic distillation using Dean-Stark apparatus. IR ν_{max}: 3507, 2927, 2856, 1744, 1465, 1377, 1295, 1238, 1153, 1125, 1051, 1012, 723, 666, 652 cm⁻¹. Found: C, 66.63; H, 9.72 %. ¹H NMR (CDCl₃): (approximate relative intensities) δ = 0.9 (t, 3H, CH₃), 1.3 (m, 26H, CH₂), 2.3 (m, 10H, CH₂), 2.9 (s, 2H, CH₂), 3.5 (m, 5H, epoxy protons), 4.2 (m, 18H, CH₂ next to ester), 5.8 (d, trace, residual peracetic acid from epoxidation), 6.4 (d, trace, residual peracetic acid), 7.1 (m, trace, residual unepoxidised C=C). ¹³C NMR (CDCl₃): δ = 14.1, 17.3, 17.6, 17.7 (CH₃); 22.5, 24.8, 26.6, 27.8, 28.9, 29.0, 29.1, 29.2, 29.4, 29.5, 29.7, 31.6, 31.8, 34.0 (CH₂); 46.4, 46.5, 48.6 (CH₂ next to ester); 54.3, 57.2 (epoxy); 64.9 (CH₂ next to ester); 128.0, 128.9, 129.5, 129.8 (C=C); 171.7, 172.1, 173.1 (C=O).

3.4.3.3 Effect of catalyst on Boltorn E1

Boltorn E1 (2.5 g, 0.24 mmol) was dissolved in ethanol (50 cm³) and the resultant solution divided into three equal aliquots. Acetic acid (0.10 g, 1.6 mmol) was added to one aliquot, hydrochloric acid (0.06 g, 1.6 mmol) to the second, the third acted as a control. None of the solutions had gelled after 2 weeks at room temperature. IR ν_{max} (all three solutions): 3474, 2927, 2856, 1742, 1467, 1378, 1240, 1126, 1012 cm⁻¹.
3.4.3.4 Modification of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate

3-(Triethoxysilyl)propyl isocyanate (0.47 g, 1.9 mmol) and 1,8-diazabicyclo(5.4.0)undec-7-ene (0.016 g, 0.11 mmol) were added to the dried solution of Boltorn E1 in toluene, which was then refluxed for 1 hour with an MgSO4 guard tube. The toluene was removed by rotary evaporation to give a pale yellow viscous liquid. IR (oil) v_max: 3507, 2927, 2856, 1744, 1697, 1655, 1468, 1374, 1295, 1241, 1158, 1119, 1080, 1012, 958, 723, 666, 652 cm⁻¹. Calculated: C, 63; H, 10; N, 1 % (approximate values as the exact composition of the hybrid is not known); found: C, 56.10; H, 8.74; N, 1.14 %.

3.4.3.5 Hydrolysis and condensation in the absence of TEOS/TMOS

The resultant pale yellow viscous liquid was redissolved in ethanol (50 cm³). Hydrolysis of the silane groups was carried out by the addition of water (0.34 g, 19 mmol) and acetic acid (0.018 g, 2.9 mmol) and the reaction mixture stirred at room temperature for 16 hours. Ethanol was removed by rotary evaporation and the product dried under vacuum to give a viscous yellow liquid. IR v_max: 3387, 2927, 2856, 1744, 1700, 1655, 1598, 1547, 1468, 1380, 1295, 1238, 1162, 1120, 1080, 1015, 958, 785, 770 cm⁻¹. ¹H NMR (CDCl₃): (approximate relative intensities) δ = 0.9 (m, 10H, CH₃), 1.2 (m, 63H, CH₂), 2.3 (m, 5H, CH₂), 2.9 (s, 2H, CH₂), 3.7 (m, 7H, epoxy protons), 4.2 (m, 11H, CH₂ next to ester). ¹³C NMR (CDCl₃): δ = 14.0, 14.1, 17.3, 17.6, 17.7, 18.3 (CH₃); 22.5, 22.6, 24.8, 25.3, 26.6, 27.8, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.7, 31.6, 31.8, 34.0 (CH₂); 46.4, 46.5, 48.6 (CH₂ next to ester); 54.2, 54.3, 57.0, 57.2, 58.4, 58.9 (epoxy); 64.4, 64.9 (CH₂ next to ester); 171.8, 172.1, 173.1 (C=O).

3.4.3.6 Modification of Boltorn E1 with 3-(triethoxysilyl)propyl isocyanate in ethanol

Boltorn E1 (2.5 g, 0.24 mmol) was dissolved in ethanol (50 cm³) and dried with molecular sieves (1/16 inch) for 40 hours at room temperature. The solution was decanted in a dry nitrogen atmosphere, and 3-(triethoxysilyl)propyl isocyanate (0.62 g, 2.5 mmol) and 1,8-diazabicyclo(5.4.0)undec-7-ene (0.016 g, 0.11 mmol) added. The mixture was stirred for 30 minutes at 50 °C under an inert atmosphere. IR v_max: 3396, 2975, 2929, 1742, 1695, 1652, 1457, 1382, 1252, 1090, 1050, 961, 882, 764, 646 cm⁻¹.
An alkoxysilane solution consisting of TEOS (2.31 g, 11.1 mmol), ethanol (0.579 g, 12.6 mmol), water (0.641 g, 35.6 mmol) and hydrochloric acid (0.054 g, 1.48 mmol) was prepared. The alkoxysilane solution was added to modified Boltorn E1 and stirred at room temperature. After thirty minutes a translucent gel was formed.

3.4.3.7 Addition of alkoxysilane solution

TEOS/acetic acid

To the product of section 4.3.3 was added a solution of TEOS (3.71 g, 17.9 mmol), water (5.50 g, 306 mmol) and acetic acid (0.29 g, 4.8 mmol) in ethanol (50 cm³). The reaction mixture was stirred at room temperature for 16 hours; ethanol was removed by rotary evaporation and the product dried under vacuum to give a pale yellow solid. Calculated: C, 47; H, 8; N, 1 % (approximate values as the exact composition of the hybrid is not known); found: C, 38.78; H, 6.23; N, 0.71 %.

TMOS/acetic acid

To the product of section 4.3.3 was added a solution of TMOS (2.71 g, 17.9 mmol), water (5.50 g, 306 mmol) and acetic acid (0.29 g, 4.8 mmol) in ethanol (50 cm³). The reaction mixture was stirred at room temperature for 16 hours; ethanol was removed by rotary evaporation and the product dried under vacuum to give a pale yellow solid. ²⁹Si NMR (solid state): δ = -60.7 (Si-C, T), -101.0 (Si-O, Q³), -109.6 (Si-O, Q⁴). ¹³C NMR (solid state): δ = 173.0, 159.2, 65.4, 47.0, 32.3, 29.9, 25.3, 23.2, 17.9, 14.5, 10.0. Calculated: C, 47; H, 8; N, 1 % (approximate values as the exact composition of the hybrid is not known); found: C, 38.68; H, 6.22; 0.81 %.

TEOS/hydrochloric acid

To the product of section 4.3.3 was added a solution of TEOS (3.71 g, 17.9 mmol), water (5.50 g, 306 mmol) and hydrochloric acid (0.17 g, 4.8 mmol). The reaction mixture was stirred at room temperature for 16 hours; ethanol was removed by rotary evaporation and the product dried under vacuum to give a pale yellow solid. IR (solid) νmax: 3371, 2927, 2856, 1743, 1666, 1536, 1467, 1377, 1292, 1241, 1123, 1071, 1017, 947, 777, 723, 607, 440 cm⁻¹. ²⁹Si NMR (solid state): δ = -62.1 (Si-C, T), -100.7 (Si-O, Q³), -107.4 (Si-O, Q⁴). ¹³C NMR (solid state): δ = 172.7, 158.0, 65.4, 47.1, 32.3, 29.9, 23.2, 17.8, 14.5. Calculated: C, 47; H, 8; N, 1 % (approximate values as the exact composition of the hybrid is not known); found: C, 40.63; H, 6.68; N, 0.59 %.
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**TMOS/hydrochloric acid**

To the product of section 4.3.3 was added a solution of TMOS (2.71 g, 17.9 mmol), water (5.50 g, 306 mmol) and hydrochloric acid (0.17 g, 4.8 mmol) in ethanol (50 cm$^3$). The reaction mixture was stirred at room temperature for 16 hours; ethanol was removed by rotary evaporation and the product dried under vacuum to give a pale yellow solid. IR (solid) $v_{\text{max}}$: 3388, 2927, 2856, 1740, 1649, 1536, 1465, 1377, 1289, 1125, 1054, 938, 785, 723, 573, 431 cm$^{-1}$. Calculated: C, 47; H, 8; H, 1 % (approximate values as the exact composition of the hybrid is not known); found: C, 38.08; H, 6.52; N, 0.77 %.

**3.4.3.8 Hybrid synthesis in the absence of 3-(triethoxysilyl)propyl isocyanate**

To the product of section 4.3.2, azeotropically dried Boltorn E1 (2.5 g, 0.24 mmol), was added a solution of TEOS (3.71 g, 17.9 mmol), water (5.50 g, 306 mmol) and acetic acid (0.29 g, 4.8 mmol) in ethanol (50 cm$^3$). The mixture was stirred using a magnetic stirrer until the Boltorn E1 dissolved and then in an ultra-sonic bath for 16 hours. The solvent was removed by rotary evaporation and the sample dried in a vacuum oven. The product was two phase and consisted of a white solid and a pale yellow liquid. IR (liquid) $v_{\text{max}}$: 3519, 2933, 1743, 1467, 1378, 1155, 1012 cm$^{-1}$; IR (solid) $v_{\text{max}}$: 3214, 2918, 2138, 1642, 1395, 1155, 1093, 969 cm$^{-1}$.

**3.4.3.9 Increased TEOS concentration**

To the product of section 4.3.4 was added a solution of TEOS (17.6 g, 84.6 mmol), water (22.9 g, 1.27 mol) and acetic acid (1.19 g, 19.8 mmol) in ethanol (150 cm$^3$). The reaction mixture was stirred with a magnetic stirrer for 17 hours and then in an ultra-sonic bath for 6 hours. Ethanol was removed by rotary evaporation and the product dried under vacuum to give an off-white solid. IR (solid) $v_{\text{max}}$: 3450, 2921, 2855, 1743, 1460, 1377, 1303, 1233, 1155, 1119, 1082, 723 cm$^{-1}$. Calculated: C, 24; H, 4; N, 0.4 % (approximate values as the exact composition of the hybrid is not known); found: C, 18.11; H, 3.61; N, 0 %.

**3.5 References**


Chapter 4: Emulsion method of hybrid synthesis
4.1 Introduction

The conventional hydrolytic sol-gel method described in Chapter 3 did not result in the synthesis of a particulate product. On drying, the sol initially formed agglomerated to become a monolith. Therefore, this hybrid could not be satisfactorily dispersed in a matrix resin.

Stöber, Fink and Bohn have developed a method for the synthesis of monodisperse, spherical silica particles [1]. This route involves the hydrolysis of a tetraalkoxysilane in a basic solution of water and alcohol. The high pH and a high ratio of water to alkoxy silicone both promote condensation, favouring the formation of particles rather than an extended gel [2]. It was hoped that this method, which has been used successfully to form silica particles, could be adapted to the synthesis of hybrid particles.

A sodium silicate sol has been used as the starting point for the method described above [3] to act as seeds around which silica can grow. The alkoxy silicone was added to the pre-formed sol; hydrolysis and condensation yielded silica particles. Therefore, it may be hypothesised that the use of an organic nucleus, rather than sodium silicate, could lead to the formation of hybrid particles. Goller and Vincent [4] have successfully used such a method for the formation of particles with a PDMS core and a silica shell.

An alternative route to the synthesis of hybrid nano-particles, based on that described above, was identified. It made use of an emulsion of Boltorn E1 as its starting point. If the HBP molecules could be suspended as a molecular dispersion in a liquid [4] then a silica network could be precipitated around each molecule. Addition of an alkoxy silicone under basic conditions would allow the precipitation of silica. It was hoped that the Boltorn E1 molecules could act as nuclei for the formation of the inorganic phase. Hence, the formation of core-shell hybrid particles may be possible.

Base-catalysed silane hydrolysis is a very fast reaction [2]; it was hoped that hydrolysis and condensation of silica would occur around individual polymer molecules before self-nucleation of the inorganic phase occurred. In addition, base-catalysed hydrolysis of a silane yields negatively charged particles with Si-O' functionality, which repel each other. This repulsion would favour the formation of a molecular dispersion of silica coated Boltorn E1 molecules, rather than
interparticular condensation. If a discrete silica network could be precipitated around each molecule, and the particles successfully isolated, dispersion of the hybrid in an epoxy resin as a nano-scale additive might be achieved.

4.2 Results and discussion

4.2.1 Formation of a stable emulsion of Boltorn E1

Owing to the lack of success in achieving a particulate product using the conventional hydrolytic sol-gel method, an emulsion polymerisation route was developed.

The use of water as a medium for the suspension was investigated (Boltorn E1 does not dissolve in water). A high concentration of water favours condensation of silica into compact structures and so encourages particle formation [2]. The addition of TEOS (and ethanol as a co-solvent) to the emulsion, followed by its hydrolysis and condensation will result in the formation of silica. The HBP droplets have the potential to act as nuclei for the precipitation of silica, so allowing the formation of core-shell hybrid products. It was decided to employ a basic catalyst for hydrolysis of the alkoxyisilane, as used in the Stöber synthesis [1], in order to favour the formation of a stable sol.

4.2.1.1 Preparation of the emulsion

Boltorn E1 was added to water at a concentration of 1 % by volume (bv). Vigorous shaking did not lead to the formation of a stable emulsion; the organic material tended to agglomerate. Ammonium hydroxide was added to the reaction mixture to give a pH of 10. In this case, a stable aqueous emulsion of Boltorn E1 was formed on shaking. The relative pK_a of the Boltorn E1 hydroxyl groups (the pK_a is not known but is assumed to be similar to that of ethanol, which is 16 [5]) and pK_b of ammonia (pK_b 9.25 [6]) show that ammonia would be unable to deprotonate Boltorn E1. Such deprotonation would result in negatively charged organic molecules that would repel each other and so favour a molecular dispersion. Despite the inability of ammonia to deprotonate the hydroxyl groups it would cause an increase in their polarity. This increased polarity would allow more favourable polar and hydrogen bonding
interactions to be formed between Boltorn E1 and water, accounting for the enhanced dispersibility at high pH.

Boltorn E1 was dispersed as a dilute emulsion (1 % bv Boltorn E1, 1 % bv aqueous ammonium hydroxide, 98 % bv deionised water), in order to favour the formation of hybrid particles. If the Boltorn E1 molecules were present in high concentration the incipient hybrid particles would be close together. The further apart the growing particles the more likely that they will remain individual core-shell particles and the less likely a continuous silica network will be formed.

4.2.2 Formation of the hybrid sol

Ethanol was added to the aqueous emulsion of Boltorn E1, prior to addition of the alkoxysilane. The alcohol acted as a co-solvent for water and the alkoxysilane. Hydrolysis of TEOS is comparatively rapid at pH10 [2]. Rapid hydrolysis may mean that, rather than growing around the Boltorn E1 molecules, nucleation of silica particles could occur to a significant degree. TEOS, rather than TMOS, was employed as the inorganic silica source because of its slower reaction rate. The more rapid nature of TMOS hydrolysis may favour the self-nucleation of silica rather than its growth around the Boltorn E1 nuclei. In order to disfavour self-nucleation of silica, TEOS was added in a slow, dropwise manner to the reaction mixture. This maintained a low concentration of silane with respect to Boltorn E1. In addition, in order to prevent particulate impurities from acting as nucleation sites for the growth of silica particles, all glassware was thoroughly cleaned prior use.

The IR spectrum of the sol revealed absorptions due to Boltorn E1 and to silica (figure 4.1). The Si-O stretching absorptions were seen at approximately 1040 cm\(^{-1}\) and 875 cm\(^{-1}\). The frequency of the carbonyl absorption at 1738 cm\(^{-1}\) was reduced relative to that of unmodified Boltorn E1 on formation of the sol. The reasons for this are discussed in section 2.2.1.
4.2.2.1 The role of ammonium hydroxide

In order to investigate the role of ammonium hydroxide in the emulsification of Boltorn E1, the organic polymer was dispersed in water at pH 7. The emulsion proved less stable than that formed at pH 10, with Boltorn E1 agglomerating on standing to form droplets several millimetres in diameter. Ammonium hydroxide (required to catalyse the hydrolysis of the alkoxysilane) was added after the alcohol and immediately prior to the addition of TEOS.

After addition of TEOS, the product had a larger particle size than that formed when the emulsion was prepared at pH 10, with discrete particles being clearly visible by eye and a proportion of the HBP forming droplets several millimetres in diameter. Therefore, it was concluded that the presence of ammonia during the emulsification process was vital for the formation of a sub-micron sized product. The IR spectra of the droplets and the sol are compared in figure 4.2. The sol and the droplets were separated by decanting the sol from the reaction vessel. The droplets showed absorptions corresponding to Boltorn E1 and to water (figure 4.3). The IR spectrum of the sol displayed absorptions corresponding to both Boltorn E1 and silica, and appeared very similar to that of the sol prepared at pH 10 (figure 4.1). This suggests that a small amount of Boltorn E1 had been emulsified and had associated with silica (the sol) but that not all of the HBP had been successfully dispersed (the
droplets). Therefore, in order to emulsify all of the organic phase it must be dispersed in water at high pH.

**Figure 4.2:** IR spectra of sol and droplets produced when Boltorn E1 was dispersed at pH 7 (TEOS has been added)

**Figure 4.3:** IR spectra of droplets from figure 4.2 and Boltorn E1
The position of the carbonyl absorption corresponding to the polyester groups in the IR spectrum of the bulk sol differed from that of the droplets and of Boltorn E1. The absorption had moved from 1738 cm\(^{-1}\) for Boltorn E1 to 1639 cm\(^{-1}\) for the sol; only a tiny absorption was seen at this position in the IR spectrum of the droplets (figure 4.3). This shift was also observed in the sol produced when Boltorn E1 was dispersed at pH 10 (figure 4.1). The shift may be due to enolisation of the polyester carbonyl groups. Keto-enol tautomerism [5] is a proton transfer equilibrium which, because of the weakening of the carbonyl bond, leads to a reduction in its observed resonant frequency. The basic reaction conditions catalyse the enolisation reaction. The base abstracts a proton from the \(\alpha\) carbon to yield an anion. The anion is a resonance stabilised species (figure 4.4), its negative charge being shared by the \(\alpha\) carbon and the carbonyl oxygen. A water molecule then acts as a Brønsted acid to transfer a proton. The presence of the enol form would enhance the formation of a stable emulsion at pH 10 with respect to the keto form by polarisation of its hydroxyl groups (section 2.1.1). Enolisation may have occurred in the dispersed material rather than the droplets as the former had a greater surface area able to interact with water and the base.

\[
\begin{align*}
\text{RCH} & \xrightarrow{\text{slow}} \text{RCH} - \text{CR'} + \text{H}_2\text{O} \\
\text{Resonance structure of conjugate base} \\
\text{RCH} & \xrightarrow{\text{fast}} \text{RCH} - \text{CR'} + \cdot\text{OH}
\end{align*}
\]

*Figure 4.4: Base catalysed enolisation [5]*
4.2.3 Drying the sol

4.2.3.1 Centrifugal sedimentation

Two methods for the isolation of the hybrid particles were investigated. The first of these, centrifugal sedimentation, resulted in gelation of the product and, therefore, was not pursued. It is assumed that this was due to interparticulate condensation of unreacted silanol and alkoxy silane functionality as the particles became closer together.

4.2.3.2 Addition of excess water

The second method employed in the isolation of the particles was adapted from a technique reported in the literature for the separation of unmodified silica particles from the reaction mixture [7]. Ammonia and alcohol can be removed by evaporation under vacuum at constant volume, the volume being maintained by the addition of deionised water. This method was adapted to involve evaporation of the water, ammonia and ethanol under atmospheric conditions. Rather than evaporation at constant volume [7], a large excess of water was added. An aliquot of the sol was poured into a shallow dish, its pH was adjusted and double its volume of deionised water was added. The sol was allowed to dry at atmospheric temperature and pressure.

4.2.3.3 The effect of pH on the product

Sols were dried at an initial pH 7, pH 9 and 10 in order to minimise particle size with respect to basicity. White solids were obtained in all three cases. At pH 9 and pH 10 the material dried to yield opaque, white platelets, whilst the material dried at pH 7 comprised a mixture of platelets and a finely divided powder. Therefore, of these conditions, pH 7 appeared to be the most successful at inhibiting interparticulate condensation and so forming a particulate product. In all cases a thin, sticky layer remained on the surface of the drying vessel. The material could not easily be separated from the solid product for characterisation but IR spectroscopy suggested it was largely residual Boltorn E1, present as a viscous liquid. This suggested the incomplete encapsulation of the organic polymer; complete encapsulation was later achieved by increasing the concentration of TEOS (section 2.5).
It was anticipated that the material isolated after evaporation at high pH would be the most finely-divided because of interparticular repulsion of negatively charged species under basic conditions [2]. It was noted that if the pH was increased to pH 11 or above dissolution of silica could occur [2]. The material isolated at pH 9 and pH 10 was translucent and platelet-like; it appeared to have dried to a thin film that had then cracked because of shrinkage due to condensation. The material isolated at pH 7 consisted of both a fine white powder and opaque white platelets. This result was unexpected, as interparticular repulsion would be anticipated to be reduced at pH 7 compared to higher pH. This may be due to the lower rates of hydrolysis and condensation reactions at pH 7 than at higher pH [2]. Therefore, at pH 7 further particle growth may have been reduced.

4.2.3.4 Characterisation of the products

IR spectroscopy of the dried product revealed the presence of both Boltorn E1 and silica (figure 4.5). Therefore, it may be concluded that a hybrid material has been formed. Silica absorptions were observed between 1100 and 1000 cm\(^{-1}\) and 900 and 600 cm\(^{-1}\) [2].

![Figure 4.5: IR spectrum of dried hybrid](image)

Experimental results suggested that not all the organic polymer had been encapsulated. This may have been due to the addition of insufficient TEOS to coat
all of the Boltorn E1 molecules. The amount of TEOS added would equate to an average coating thickness of 0.4 nm of silica, if the Boltorn E1 molecules are assumed to be spherical and discrete. This is comparable to the thickness of a silica monolayer. However, it is extremely unlikely that TEOS would distribute itself evenly throughout the emulsion to give a perfect monolayer of silica around each HBP molecule. Therefore, the effect of increasing the amount of TEOS added to the dispersion was investigated (section 2.5).

Alternatively, the incomplete encapsulation of Boltorn E1 may be due to insufficient compatibility between the organic and inorganic phases. This would lead to phase separation, hence the observation of both a solid and a liquid product.

4.2.4 The use of a coupling agent

4.2.4.1 3-(Triethoxysilyl)propyl isocyanate

With the aim of enhancing the compatibility of the two phases, Boltorn E1 was modified with 3-(triethoxysilyl)propyl isocyanate (4.1) prior to addition of ethanol and TEOS.

![3-(Triethoxysilyl)propyl isocyanate](image)

(4.1): 3-(triethoxysilyl)propyl isocyanate

This coupling agent forms a urethane linkage with the free hydroxyl groups of Boltorn E1, whilst the silane functionality is available for condensation with TEOS. The reaction was catalysed by the tertiary amine DBU (4.2). The reaction of Boltorn E1 with this coupling agent was described in Chapter 3 section 2.1.2.

![DBU](image)

(4.2): DBU
Following the addition of ethanol and TEOS, and the resultant sol-gel process, an agglomerated product (irregular particles several millimetres in diameter) was observed. This may have been due to the presence of the tertiary amine catalyst, DBU. The amine is also able to catalyse the opening and cross-linking of the Boltorn E1 epoxy groups, using the nitrogen lone pair, leading to agglomeration of the HBP. The opened epoxy ring (figure 4.6) is able to open further epoxy rings, causing the cross-linking reaction to propagate [8].

![Figure 4.6: Epoxy ring opening via the nucleophilic nitrogen lone pair of DBU](image)

**4.2.4.2 GPTMS**

The use of an alternative coupling agent, GPTMS (4.3), was investigated. GPTMS is capable of forming favourable van der Waals interactions with Boltorn E1 through its epoxy groups, whilst the silane functional group can be hydrolysed simultaneously with TEOS and subsequently participate in the silica network formation.

![Image of GPTMS](image)

**4.3: GPTMS**

Therefore, GPTMS has the potential to act as a link between the organic and inorganic phases without the requirement of a tertiary amine as in the case of 3-(triethoxysilyl)propyl isocyanate. However, the addition of GPTMS did not significantly enhance the compatibility of the organic and inorganic phases. A liquid was again present in the product of the reaction.
GPTMS was added concurrently with TEOS and this may have hindered its compatibilising effect. It is possible that the presence of TEOS and the rapid nature of the sol-gel reaction sterically prevented the epoxy groups of GPTMS from reaching the surface of the Boltorn E1 droplets, so impairing the favourable epoxy-epoxy interactions. Pre-addition of GPTMS to allow its epoxy groups to interact with Boltorn E1 prior to the addition of TEOS may aid compatibility.

Covalent bonding may further enhance the compatibility of GPTMS with Boltorn E1. This may be possible by reducing the pH of the emulsion after the addition of GPTMS. Under acidic conditions the epoxy groups will open (figure 4.7) and cross-links between Boltorn E1 and GPTMS may form. This covalent bonding would provide a link between the organic and inorganic phases. However, if the pH was lowered the silane groups of GPTMS may be hydrolysed.

Alternatively, the use of a mercaptan coupling agent, HS-R'-Si(OR)₃, which could bond to Boltorn E1 by nucleophilic opening of its epoxide rings by the sulfur lone pair, could lead to enhanced compatibility. This coupling agent would form covalent bonds with the organic HBP under conditions that avoid catalysing its polymerisation. The silane groups of the coupling agent would be available to be incorporated into the silica network formed on the addition of TEOS.

![Figure 4.7: Formation of a β-substituted alcohol by acid-catalysed epoxy ring opening (Y represents a nucleophile, which may be a solvent molecule)]
4.2.5 Increasing the concentration of TEOS

It may be calculated that the concentration of TEOS added to Boltorn E1 was sufficient to give a silica shell of average thickness 0.4 nm, assuming the Boltorn E1 molecules are spherical and discrete. This value is similar to the thickness of a monolayer of silica (0.3 nm). However, it is statistically very unlikely that perfect monolayers of silica would be formed around HBP molecules. If a higher concentration of TEOS were employed, the formation of a product in which Boltorn E1 was completely encapsulated would be more likely. Therefore, the use of a concentration of TEOS to give a silica shell of calculated average thickness 1 nm was investigated.

Increasing the concentration of TEOS proved successful. The samples exhibited more complete encapsulation of Boltorn E1 than the materials with lower silica content. Solid products were formed with no sticky layer present. Therefore, it was inferred that core-shell particles, in which Boltorn E1 was coated in a layer of silica, had been formed. The complete encapsulation of Boltorn E1 accounted for the solid product observed.

4.2.5.1 TEM

In order to determine whether aggregation of the particles had occurred during the drying process, electron microscopy was carried out before and after isolation, and the particle sizes compared. A series of sols, synthesised with the higher concentration of TEOS, was examined by TEM (figure 4.8). The effects of increasing the concentration of alcohol added, prior to TEOS addition, and of varying the nature of this alcohol were investigated. TEM revealed that in all cases discrete, spherical particles had been formed. The mean particles diameters observed are given in table 4.1.

The alcohol was added to the reaction mixture to act as a co-solvent for TEOS and water. It has been shown [1, 9] that in general shorter chain alcohols yield smaller silica particles. Therefore, the effect on particle size of substituting methanol for ethanol was investigated (table 4.1). Boltorn E1 is soluble in ethanol and methanol and as such the concentration of alcohol added must be low to maintain the emulsion of HBP droplets. However, the alcohol formed the reaction medium for
silica growth and so a certain volume was required. It has been shown [4, 10] that silica growth will occur when ethanol is present at concentrations of approximately 25 to 60 % bv. Therefore, the effect on particle size of increasing the alcohol concentration from 25 % bv to 50 % bv was investigated.

![Image: Transmission electron micrograph of hybrid particles (25% bv ethanol)]

**Figure 4.8: Transmission electron micrograph of hybrid particles (25% bv ethanol)**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Alcohol concentration (% bv)</th>
<th>Mean particle diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>25</td>
<td>0.38 (st dev 0.29)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>50</td>
<td>2.03 (st dev 0.14)</td>
</tr>
<tr>
<td>Methanol</td>
<td>25</td>
<td>0.38 (st dev 0.23)</td>
</tr>
</tbody>
</table>

**Table 4.1: Mean diameter and standard deviation (st dev) of hybrid particles**

Changing the alcohol from ethanol to methanol appeared to have no effect on the mean particle size. No significant difference in particle size distribution was observed. Increasing the concentration of alcohol added can be seen to increase the particle size. The total number of particles visible on the transmission electron microscope grid was correspondingly diminished with respect to the other samples. The standard deviation for the 25 % alcohol samples was large, a large range of particle sizes was observed. This suggested some degree of agglomeration, either of the organic polymer before addition of TEOS or of the hybrid particles after
addition of TEOS. However, some very small particles, of approximate diameter 1 nm, were also present in the 25 % alcohol samples. Owing to their small size these particles were likely to be pure silica; the diameter of a Boltron E1 molecule, assuming it is spherical and discrete, is 3.2 nm. Therefore, a particle of 1 nm diameter could not be expected to contain a Boltron E1 core. These very small products were not included in the calculation of mean particle size.

4.2.5.2 Isolation of the product

Addition of excess water, followed by drying the sols at room temperature, yielded brittle, opaque white platelets that readily formed a powder on grinding. Therefore, it can be inferred that the particles observed by TEM had agglomerated during the drying process. SEM of the materials was carried out in order to elucidate the degree of agglomeration and morphology of the product.

The hybrid sols were isolated by the addition of excess water followed by evaporation of solvent at room temperature. Prior to drying, the reaction mixtures were acidified to pH 7, as neutral conditions were shown to yield a more finely-divided product than a higher pH in section 2.3.3.

4.2.5.3 SEM

SEM of the dried products appeared to show particles of diameter of the order of 1 μm contained within a thick gel layer (figure 4.9). This suggested that, as the particle concentration increased on evaporation of the solvent, interparticular condensation occurred via the residual alkoxy silane or silanol functionality at the surface of the particles. These unreacted groups were able to hydrolyse and condense, forming a gel matrix.

The TEM results (table 4.1) proved that the formation of sub-micron particles was possible using this synthetic method. SEM studies (figure 4.9) suggested that the hybrids agglomerated during the drying process.
4.2.6 Addition of a capping agent

4.2.6.1 Methoxytrimethylsilane

In order to reduce particle agglomeration during drying, the use of a reagent to alter the surface functionality of the particles, a 'capping agent', was investigated. It was hypothesised that if the residual alkoxysilane and silanol groups at the surface of the particles could be modified in such a way as to render them unable to react with each other, interparticular condensation could be prevented. In the pursuit of this aim, a monofunctional alkoxysilane was added to the sol prior to isolation. The alkoxysilane chosen was methoxytrimethylsilane (4.4).

\[
\text{(4.4): Methoxytrimethylsilane}
\]
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The methoxy group of this silane was able to react with the surface functional groups of the sol particles. As there is only one methoxy group per silane molecule the particles become effectively capped with methyl groups. These methyl groups would then be unable to condense with unreacted silanol and alkoxysilane groups from neighbouring particles and so interparticular agglomeration would be prevented.

A potential side reaction could be the condensation of the capping agent with itself to form a dimeric product (figure 4.10). The formation of this by-product was disfavoured by the slow addition of methoxytrimethylsilane to the sol. Slow addition ensured a low concentration of unreacted capping agent with respect to particles, hence the capping reaction was statistically more likely than dimerisation.

![Dimerisation of methoxytrimethylsilane](image)

**Figure 4.10: Dimerisation of methoxytrimethylsilane**

4.2.6.2 Addition of methoxytrimethylsilane to the hybrid sol

Methoxytrimethylsilane was added to a pre-formed hybrid sol. This sol was synthesised using the higher concentration of TEOS, such that when condensed it would theoretically be equivalent to a silica shell of 1 nm average thickness, assuming the Boltorn E1 molecules were spherical and discrete.

Methoxytrimethylsilane was added to the sol at a molar concentration corresponding to two-thirds that of TEOS. As a 1 nm thick silica shell may be calculated to correspond to an approximate average of 3 layers of silica tetrahedra, one third of the silica formed by TEOS would be expected to be at the particle surfaces. Therefore, assuming two unreacted silanol or alkoxysilane group per surface TEOS molecule, the amount of methoxytrimethylsilane added would theoretically be sufficient to 'cap' the particles. There are many approximations and assumptions involved in the calculation of this amount; as such it is rather arbitrary. Therefore, the concentration of methoxytrimethylsilane was varied to optimise its concentration with respect to minimising particle size (section 2.8).
On stirring the reaction mixture at room temperature, a fine white suspension was formed. Drying the sol at pH 7 after the addition of excess water resulted in the formation of a finely-divided white powder. Macroscopic particle agglomeration, and hence platelet formation, had not occurred. The isolated product was characterised by SEM, IR spectroscopy, DSC and TG analysis.

4.2.6.3 SEM

SEM of the dried product revealed spherical particles of approximate diameter 200 nm. This suggested that methoxytrimethylsilane may have, to a degree, inhibited particle aggregation during the drying process. The particle size was a little smaller than that observed by TEM of the sol without addition of methoxytrimethylsilane (table 4.1) suggesting the 'capping agent' inhibited interparticular condensation within the sol. However, SEM appeared to show a degree of particle clumping (figure 4.11). It is possible that this was an artefact of the microscopic technique, static charging causing the particles to agglomerate. A more pragmatic appraisal of particle agglomeration would come from microscopy of blends of the additive in an epoxy matrix, as this was the application for which the hybrid was intended.

Figure 4.11: Scanning electron micrograph of hybrid capped with methoxytrimethylsilane
4.2.6.4 IR spectroscopy

The IR spectrum of the powder contained absorptions corresponding both to Boltorn E1 and to silica (figure 4.12). This implied that Boltorn E1 had been encapsulated; the absence of a liquid product or sticky layer in the reaction vessel suggested the complete encapsulation of the organic phase. The IR spectrum of the capped hybrid showed a small absorption corresponding to enol formation (section 2.2.1). The main carbonyl absorption was observed at 1738 cm⁻¹, the same frequency as the carbonyl absorption of unmodified Boltorn E1. The degree of base-catalysed enolisation was reduced with respect to the uncapped hybrid (figure 4.2); this may have been caused by the capping agent shielding the organic polymer core of the hybrid from the solvent. Enolisation would be expected to have occurred prior to addition of the capping agent; the keto-enol equilibrium may have moved towards the keto form on condensation of methoxytrimethylsilane.

![IR spectrum](image)

**Figure 4.12: IR spectrum of the hybrid capped with methoxytrimethylsilane**

Whilst the IR spectrum confirmed the hybrid nature of the product, it is possible that some of the particles were purely inorganic in nature, formed by the nucleation and growth of silica from TEOS (as in the very small particles observed by TEM (section 2.5.1). It may be possible to separate the silica particles from the hybrid by differential centrifugation, as they will have different densities. Silica has a density of approximately 2.20 g.cm⁻³ [2], whereas Boltorn E1 has a density of 1.04 g.cm⁻³ [11].
Therefore, it may be inferred that the hybrid particles will have a lower density than any pure silica particles present.

4.2.6.5 TG analysis

TG analysis of the product revealed a three-stage decomposition (figure 4.13). As the hybrid was raised above room temperature, up to approximately 100 °C, a small mass loss (approximately 2.5 %) was observed. It is likely that this was due to condensation of residual silanol and alkoxysilane groups, resulting in the release of methanol, ethanol and water.

A further decomposition occurred between 175 °C and 250 °C (approximately 7 mass %). This loss was likely to be due to the loss of the methyl groups of the capping agent. TG analysis of condensed methoxytrimethylsilane alone showed a mass loss at 200 °C, corresponding to the loss of the organic methyl groups. The theoretical mass loss due to the methyl groups would be 12 %. The lower value observed may be due to incomplete condensation of methoxytrimethylsilane, the uncondensed material being lost at its boiling point of 55 to 57 °C. Alternatively, it may be due to the incomplete condensation of TEOS, the loss of ethanol and water would lead to the methyl groups representing a smaller mass percent than that calculated.

The final mass loss at around 380 °C was probably due to Boltorn E1. TG analysis of Boltorn E1 alone revealed a mass loss at 380 °C. At 1000 °C approximately 70 % of the mass of the hybrid remained. This correlated well with the theoretical composition of the hybrid (calculated to be 70 % inorganic).
4.2.6.6 DSC

DSC of the hybrid (figure 4.14) did not reveal an exotherm due to the cross-linking of the epoxy groups of Boltorn E1 (c.f. DSC of Boltorn E1 (figure 4.15)). This observation concurred with the hypothesis that Boltorn E1 had been encapsulated by silica. If the Boltorn E1 molecules were free to move and cross-link an exotherm would have been observed. The lack of an exotherm suggested that the molecules were held apart from each other (or that cross-linking into small assemblies had occurred prior to the analysis) and were unable to cross-link. The encapsulation of Boltorn E1 by silica would lead to a solid product in which the organic molecules were sterically prevented from reacting and the core-shell nature of the hybrid particles may be inferred.

The endotherm observed in the DSC thermogram at around 80 °C was likely to be due to the further condensation of silica leading to the evaporation of volatile molecules, whilst that at 200 °C may correspond to the thermolysis of the methoxytrimethylsilane methyl groups (c.f. TG thermogram, figure 4.13).
4.2.7 The effect of pH on morphology

The effect of varying the pH during the drying process on hybrid morphology was investigated. Drying at pH 7 had produced a finely-divided particulate product. It had
been assumed that a high pH during the drying process would favour the isolation of a particulate product. This was because the silica shells of the particles would carry a negative charge [2] and so would repel each other. Therefore, the hybrid sol was dried at pH 10. Here, an aliquot of the sol was dried at pH 2 as this represents the isoelectric point of silica [2] and, therefore, the point of lowest electron mobility. As such, interparticular condensation may be at a minimum at this pH.

SEM of the dried products revealed that drying the sol at pH 2 yielded smaller particle size than pH 7 or pH 10 (figure 4.16). Individual particles of less than 100 nm appeared to have been formed but to have aggregated to form clumps approximately 2 µm in diameter. At pH 10 the product appeared to consist of particles contained within a gel matrix (figure 4.17).

![Capped hybrid dried at pH 2](image)

**Figure 4.16: Capped hybrid dried at pH 2**
4.2.8 Varying the concentration of methoxytrimethylsilane

The concentration of methoxytrimethylsilane added was varied in order to determine its effect on the morphology of the dried product. The amount of the capping agent added was doubled in one aliquot of the sol and halved in another with respect to the amount used in section 2.6. The sols were dried in excess water after acidification to pH 2. The material synthesised using the higher concentration of trimethoxymethylsilane dried to form a free-flowing powder. The lower concentration of capping agent yielded platelets of an opaque, white solid (figure 4.19). This latter result suggested that the concentration of trimethoxymethylsilane added was not sufficient to prevent interparticular condensation.

If a high concentration of methoxytrimethylsilane were added it would be present in excess. In this case it may condense with itself and so dimers would be present as an impurity (figure 4.10). Therefore, the minimum concentration of
methoxytrimethyisilane to yield a free-flowing powder on drying the sol should be employed.

4.2.8.1 SEM

SEM of the three materials with varying concentrations of methoxytrimethyisilane was carried out (figures 4.18 to 4.20). SEM has revealed agglomerated products (figure 4.16); it may be that some of this agglomeration was caused by static charging in the microscope. In order to disperse the particles as well as possible on the microscope stub, the dried material was dispersed in acetone and a drop placed on the stub. The sample was dried under a stream of compressed air. This technique revealed a finer dispersion of particles (figures 4.18 and 4.19). Individual particles, smaller than 100 nm in diameter, appear to have agglomerated to form clumps a few hundred nanometres in diameter, in the case of the middle concentration of methoxytrimethyisilane (figure 4.18). These particles appear flat because of static charging.

Figure 4.18: Dried hybrid made using methoxytrimethyisilane at two-thirds the molar concentration of TEOS
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Figure 4.19: Dried hybrid made using methoxytrimethylsilane at one-third the molar concentration of TEOS

Figure 4.20: Dried hybrid made using methoxytrimethylsilane at four-thirds the molar concentration of TEOS
4.2.8.2 \( ^{29}\text{Si} \) NMR spectroscopy

The dried hybrids were analysed using solid state \( ^{29}\text{Si} \) NMR spectroscopy. For all the concentrations of methoxytrimethyisilane tested the degree of condensation was high. The samples were analysed before and after heating at 300 °C for one hour, to see if the degree of condensation increased. The increase in size of the Q\(^4\) peaks was very small (table 4.2), except in the case of the middle concentration of methoxytrimethyisilane. TG analysis of this material showed a mass loss on heating to 100 °C, which was attributed to further condensation of unreacted silanol and alkoxy silane groups. The observation by \( ^{29}\text{Si} \) NMR spectroscopy of an increase in the size of the Q\(^4\) peak agrees with this hypothesis of further condensation.

In all cases the Q\(^4\) peak was approximately four times the size of the Q\(^3\) peak. A peak corresponding to the methoxytrimethyisilane silicon was resolved at approximately 13 ppm. This peak was only about one ninth the size of the combined Q peaks for all concentrations of capping agent. This was smaller than the theoretical proportions of methoxytrimethyisilane, which was added at one-third, two-thirds or four-thirds the molar concentration of TEOS.

<table>
<thead>
<tr>
<th>Size of peak (%)</th>
<th>Concentration of MeOSiMe(_3) relative to TEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/3</td>
</tr>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>MeOSiMe(_3)</td>
<td>11.0</td>
</tr>
<tr>
<td>Q(^2)</td>
<td>-</td>
</tr>
<tr>
<td>Q(^3)</td>
<td>17.4</td>
</tr>
<tr>
<td>Q(^4)</td>
<td>71.6</td>
</tr>
</tbody>
</table>

*Table 4.2: \( ^{29}\text{Si} \) NMR spectroscopy of dried hybrids with varying concentration of methoxytrimethyisilane, before (A) and after (B) heating at 300 °C for 1 hour*

4.2.8.3 BET analysis

The specific surface area of the samples was determined by gas/vapour adsorption. This can be calculated from the volume of gas adsorbed at a given partial pressure using the BET isotherm. BET analysis of the hybrid products synthesised using varying concentrations of methoxytrimethyisilane was carried out (table 4.3). A literature value of specific surface area reported for silica colloids dried in air for 16 hours is 182 m\(^2\)/g\(^{-1}\) [12]. The higher value observed experimentally may be due to
the presence of Boltorn E1. In addition, the difference may be a result of different experimental conditions, for example the lower drying temperature used here (ambient temperature as opposed to 110 °C). A higher drying temperature would promote condensation and so increase particle size and reduce porosity, both of these effects would lead to a decrease in surface area.

<table>
<thead>
<tr>
<th>Concentration of MeOSiMe₃ relative to TEOS</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/3</td>
<td>309</td>
</tr>
<tr>
<td>2/3</td>
<td>383</td>
</tr>
<tr>
<td>4/3</td>
<td>270</td>
</tr>
</tbody>
</table>

Table 4.3: Surface area of hybrids

The BET isotherm of all three samples was of type H3 [13]. This type of isotherm is generally found for materials consisting of aggregates of particles in which the pores tend to be slit-shaped [13]. This morphology concurs with that observed by SEM (figure 4.16) in which aggregates of particles are clearly visible. The shape of the pores is not obvious but they appear to be irregular.

4.3 Conclusions

A particulate organic-inorganic hybrid has been successfully synthesised using a hydrolytic sol-gel method in the presence of an emulsion of the organic phase. The hybrid nature of the particles was confirmed by IR spectroscopy, which showed absorptions due to both Boltorn E1 and silica. Electron microscopy showed that the synthesis of particles of diameter less than 100 nm was possible but that the particles display a degree of agglomeration.

Particle agglomeration was reduced by the addition of a capping agent, which was able to react with residual silanol and alkoxy silane groups. SEM of this material, having been dispersed in acetone, showed only a small degree of particle agglomeration. The aggregates formed were sub-micron in size and individual particles were less than 100 nm in diameter.
Whilst the chemical composition of the particles was revealed by IR spectroscopy and the morphology by electron microscopy, determination of the structure of the hybrids has not been carried out and may be non-trivial. It was assumed that these particles were core-shell hybrids consisting of Boltorn E1 at their centre, surrounded by silica. However, this was simply inferred from the observation that no unencapsulated, liquid HBP remained on isolation of the particles and that the DSC thermogram of the hybrid did not show an exotherm owing to cross-linking of the epoxy groups. Direct evidence for the core-shell morphology has not yet been obtained. If it were possible to freeze fracture the particles and examine them by SEM their internal structure may be observed, although their chemical nature would not be known.

Indirect confirmation of the two-phase nature of the particles may come from surface analysis. If the surface of the particles could be shown to consist of silica then it may be inferred that the Boltorn E1 present was sequestered at the centre of the particles, as IR spectroscopy has confirmed the presence of both phases. The particle surfaces could be characterised by x-ray photoelectron spectroscopy (XPS).

The capping agent employed, methoxytrimethylsilane, is monofunctional and as such the majority of its surface is composed of methyl groups. The methoxy group must approach the hybrid particle surface closely in order to react with it. It is possible that the methyl groups sterically hinder this approach. The effect of adding a difunctional capping agent, such as dimethoxydimethylsilane (4.5) might cause less steric hindrance. It has two reactive groups and so a higher proportion of its surface is functionalised; this molecule may be more easily able to react with the hybrid particle than methoxytrimethylsilane. It is unlikely that both methoxy groups would react with different particles due to their proximity (they would be separated by an angle of approximately 109.5° and an Si-O bond length of 0.16 nm). If both groups react it would most probably be with the same particle. The steric strain at the tetrahedral silicon centre of the molecule would be great if it were bonded to two different hybrid particles, each of the order of 100 nm diameter.

4.5: Dimethoxydimethylsilane
The addition of surfactant to the hybrid sol after the capping agent might inhibit agglomeration and interparticular condensation by stabilising the particulate dispersion. The surfactant must be removed by washing with water prior to blending the particles with a resin as its presence could cause plasticisation of the resin and so impair its thermal properties [8].

4.4 Experimental

4.4.1 Instrumentation

IR spectra were recorded on a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer. IR spectra were obtained in the absorption mode at a resolution of 1 cm\(^{-1}\) and 16 scans. Solid samples were scanned as a nujol mull; solids (mull) and liquids were scanned as a thin film between 4 mm thick KBr plates. \(^{29}\)Si solid state direct polarised NMR spectroscopy was carried out on a Varian UNITY\(plus\) spectrometer against an external tetramethylsilane standard with magic angle spinning at a rate of 5000 Hz. The spectra were obtained using a 90° excitation pulse and a 240 second relaxation delay. Solution phase \(^{13}\)C and \(^{1}\)H NMR spectra were obtained in CDCl\(_3\). \(^{13}\)C NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 100 MHz and ambient temperature. \(^{1}\)H NMR spectroscopy was carried out on a Bruker DPX 400 spectrometer at 400 MHz and ambient temperature.

DSC was carried out under a nitrogen atmosphere using a TA Instruments 2920 Modulated Differential Scanning Calorimeter, with modulation at an amplitude of ±1 K, a 60 second period and an underlying ramp rate of 3 K.min\(^{-1}\). TG analysis was performed in a nitrogen atmosphere using a Perkin-Elmer TGA7 Thermogravimetric Analyzer, at a ramp rate of 10 K.min\(^{-1}\).

SEM was carried out on gold-coated samples using a LEO 1550 Field Emission Scanning Electron Microscope. TEM was carried out using a Philips 400T transmission electron microscope. Droplets of the sol were transferred to carbon-coated copper carrier grids using a glass capillary. Samples were dried for 5 minutes at 40 °C then at room temperature. BET analysis was carried out using a Coulter SA3100 series Surface Area and Pore Size Analyzer.
Chapter 4: Emulsion method of hybrid synthesis

4.4.2 Materials

Boltorn E1 was obtained from Perstorp Specialty Chemicals of Sweden via ACG. All other chemicals were obtained from Aldrich and were used as received.

4.4.3 Preparation of hybrid sol at pH 10

All apparatus was thoroughly cleaned before use to reduce secondary nucleation of silica particles. This was achieved by soaking in 4 % by mass aqueous sodium hydroxide for 12 hours, then in 14 % by mass aqueous nitric acid for 10 minutes. This was followed by rinsing with hot tap water and deionised water.

Boltorn E1 (1.04 g, 1% bv), ammonia solution (supplied as 35 weight %) (1 cm³, 1% bv) and deionised water (98 cm³, 98 % bv) were vigorously shaken for 30 seconds, then left to stand for 18 hours.

To this emulsion (100 cm³, 65 % bv) was added ethanol (46 cm³, 30 % bv) and the mixture stirred with a magnetic stirrer. TEOS (7 cm³, 5 % bv) was added dropwise at a rate of 2 cm³/h. The mixture was stirred for 24 hours at room temperature. IR (liquid) $v_{max}$: 3400, 2978, 2932, 2900, 2115, 1648, 1639, 1454, 1384, 1213, 1087, 1045, 879 cm⁻¹.

4.4.4 Emulsification of Boltorn E1 at pH 7

Boltorn E1 (1.04 g) and deionised water (98 cm³) were vigorously shaken for 30 seconds, then left to stand for 18 hours.

To this emulsion (99 cm³) was added ammonia solution (supplied as 35 weight %) (1 cm³) and ethanol (42.4 cm³) and the mixture stirred with a magnetic stirrer. TEOS (27.2 cm³) was added slowly dropwise. The mixture was stirred for 24 hours at room temperature. A white sol was formed in conjunction with pale yellow droplets, a few millimetres in diameter. IR (droplets) $v_{max}$: 3492, 2945, 2920, 2856, 1747, 1463, 1377, 1275, 1232, 1151, 1122, 1040, 1009, 878 cm⁻¹. IR (sol) $v_{max}$: 3362, 2976, 2914, 2899, 2100, 1639, 1448, 1404, 1381, 1205, 1080, 1041, 937, 874 cm⁻¹.
4.4.5 Drying the sol

The pH of an aliquot (10 cm$^3$) of the reaction mixture was adjusted to pH 7, 9 or 10 as appropriate by the dropwise addition of hydrochloric acid. Deionised water (20 cm$^3$) was added and the mixture allowed to dry at ambient temperature and pressure. The products were a white solid and a small amount of a viscous, colourless liquid. IR (solid) $\nu_{\text{max}}$: 3433, 2951, 2919, 2855, 1642, 1458, 1376, 1105, 969 cm$^{-1}$. IR (liquid) $\nu_{\text{max}}$: 3507, 2948, 2924, 2851, 1743, 1466, 1377, 1286, 1241, 1153, 1123, 1054, 1011 cm$^{-1}$.

4.4.6 Coupling agents

4.4.6.1 3-(Triethoxysilyl)propyl isocyanate

Boitorn E1 (1.5 g, 0.14 mmol) was dissolved in toluene (30 cm$^3$) and the solution dried by azeotropic distillation using Dean-Stark apparatus. IR (toluene solution) $\nu_{\text{max}}$: 3507, 2927, 2856, 1744, 1465, 1377, 1295, 1238, 1153, 1125, 1051, 1012, 723, 666, 652 cm$^{-1}$. Found: C, 66.63 %; H, 9.72 %. $^1$H NMR (CDCl$_3$): (approximate relative intensities) $\delta$ = 0.87 (t, 3H, CH$_3$), 1.25 (m, 26H, CH$_2$), 2.28 (m, 10H, CH$_2$), 2.88 (s, 2H, CH$_2$), 3.53 (m, 5H, epoxy protons), 4.18 (m, 18H, CH$_2$ next to ester), 5.81 (d, trace, residual peracetic acid from epoxidation), 6.36 (d, trace, residual peracetic acid), 7.11 (m, trace, residual unepoxidised C=C). $^{13}$C NMR (CDCl$_3$): $\delta$ = 14.05, 17.30, 17.62, 17.74 (CH$_3$); 22.54, 24.80, 26.57, 27.78, 28.87, 29.02, 29.09, 29.17, 29.38, 29.49, 29.65, 31.61, 31.81, 33.98 (CH$_2$); 46.37, 46.51, 48.63 (CH$_2$ next to ester); 54.30, 57.17 (epoxy); 64.93 (CH$_2$ next to ester); 125.97, 128.85, 129.52, 129.84 (C=C); 171.74, 172.13, 173.12 (C=O).

3-(Triethoxysilyl)propyl isocyanate (0.37 g, 1.5 mmol) and DBU (0.0096 g, 0.066 mmol) were added to the dried solution which was then refluxed for 1 hour with an MgSO$_4$ guard tube. The toluene was removed by rotary evaporation to give a pale yellow viscous liquid. IR (oil) $\nu_{\text{max}}$: 3507, 2927, 2856, 1744, 1697, 1655, 1468, 1374, 1295, 1241, 1158, 1119, 1080, 1012, 958, 723, 666, 652 cm$^{-1}$. Calculated (approx): C, 63; H, 10; N, 1 %; found: C, 56.10; H, 8.74; N, 1.14 %.
A hybrid sol was prepared from modified Boltorn E1 as in section 4.3. The product was a white solid with particle size several millimetres in diameter.

**4.4.6.2 GPTMS**

Boltorn E1 (1.04 g, 1% bv), ammonia solution (supplied as 35 weight %) (1 cm³, 1% bv) and deionised water (98 cm³, 98 % bv) were vigorously shaken for 30 seconds, then left to stand for 18 hours.

To this emulsion (100 cm³, 65 % bv) was added ethanol (38 cm³, 25 % bv) and the mixture stirred with a magnetic stirrer. TEOS (5 cm³, 3.6 % bv) and GPTMS (2 cm³, 1.4 % bv) were mixed and then added dropwise at a rate of 2 cm³.h⁻¹. The mixture was stirred for 24 hours at room temperature. The resultant sol was stirred at room temperature for 48 hours then dried at pH 7 as in section 4.5.

**4.4.7 Preparation of hybrid sol with increased TEOS concentration**

Boltorn E1 (1.04 g, 1% bv), ammonia solution (supplied as 35 weight %) (1 cm³, 1% bv) and deionised water (98 cm³, 98 % bv) were vigorously shaken for 30 seconds, then left to stand for 18 hours.

To this emulsion (100 cm³) was added ethanol (42.4 cm³, 25 % bv), methanol (42.4 cm³, 25 % bv) or ethanol (127.2 cm³, 50 % bv) and the mixture stirred with a magnetic stirrer. TEOS (27.2 cm³, 16 %, 16 % or 11 % bv) was added dropwise at a rate of 2 cm³.h⁻¹. The resultant sol was stirred at room temperature for 24 hours, then TEM carried out. IR (liquid) \(\nu_{\text{max}}\): 3400, 2978, 2932, 2900, 2115, 1648, 1639, 1454, 1384, 1213, 1087, 1045, 879 cm⁻¹.

The sols were dried as in section 4.5 at pH 7. The products were white solids. IR (mull) \(\nu_{\text{max}}\): 3508, 2941, 2918, 2905, 2849, 1734, 1647, 1456, 1375, 1094, 949, 789 cm⁻¹.
4.4.8 Addition of methoxytrimethylsilane

A hybrid sol was prepared as in section 4.3. To the sol methoxytrimethylsilane (8.47 g, 9.06 cm³, 81 mmol) was added dropwise and the sol stirred at room temperature for 16 hours.

4.4.8.1 Effect of pH on drying

The sol prepared in section 4.8 was dried at pH 10, pH 7 and pH 2 by the method described in section 4.5. The products dried at pH 7 and pH 2 were finely-divided white powders, that dried at pH 10 was an opaque white solid. IR for all three products (mull) \( \nu_{\text{max}} \): 2954, 2926, 2854, 1739, 1705, 1462, 1455, 1377, 1253, 1104, 1088, 846, 805, 797 cm⁻¹. \(^{29}\text{Si NMR (product dried at pH 2): -110.8, -101.4, -91.3, 12.6; after heating at 300 °C for 1 hour: -110.6, -101.1, 12.7.}

4.4.8.2 Variation of the concentration of methoxytrimethylsilane

Two hybrid sols were prepared as in section 4.7. To the sol methoxytrimethylsilane (4.24 g, 4.53 cm³, 41 mmol, or 16.94 g, 18.12 cm³, 162 mmol) was added dropwise and the sol stirred at room temperature for 16 hours. The sols were dried at pH 2, following the method described in section 4.5. IR for both products (mull) \( \nu_{\text{max}} \): 2951, 2920, 2864, 1734, 1705, 1458, 1376, 1249, 1105, 1080, 866, 796 cm⁻¹. 41 mmol methoxytrimethylsilane added \(^{29}\text{Si NMR: -111.0, -101.4, 12.5; after heating at 300 °C for one hour: -110.5, -101.3, 12.6. 162 mmol methoxytrimethylsilane added \(^{29}\text{Si NMR: -111.1, -102.5, 12.3; after heating at 300 °C for one hour: -111.4, -101.3, 12.5.}

4.5 References

[1] W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci., 1968, 26, 62


Chapter 5: Silica and organic-inorganic hybrids as resin additives
Chapter 5: Silica and organic-inorganic hybrids as resin additives

5.1 Introduction

The organic-inorganic hybrid particles, the synthesis of which was described in chapter 4, were blended with an epoxy resin. Commercially available silica nanoparticles were blended with the same resin [1] in order to compare the properties of the blends. The cured resins were characterised in terms of their thermal properties and fracture toughness. The hybrids synthesised using the conventional sol-gel method (as described in chapter 3) formed monolithic products rather than particles. As the aim of this work was the synthesis of hybrid nanoparticles, the addition of these monolithic materials to an epoxy resin was not investigated.

It was hoped that the properties of the organic and inorganic components of the hybrids would combine to enhance both the thermal and mechanical properties of the resin [2, 3]. Inorganic silica is thermally stable beyond the degradation temperature of the organic matrix [4]. Therefore, it was anticipated that the addition of silica might increase the thermal stability of the resin blends. It was hypothesised that resin molecules adjacent to the silica particles may be able to bond to them through unreacted silanol groups, and also that physical 'confinement' of the organic component may occur. These mechanisms may delay the thermal degradation of the organic material adjacent to the silica particles. For such thermal stabilisation to be achieved it is important that the additive is finely dispersed throughout the matrix.

The organic component of the hybrids, Boltorn E1, has been shown not to toughen the epoxy resins tested (chapter 2). However, the effects of the organic phase on the resin cannot be directly correlated with the hybrid and so the fracture toughness values of the blends were determined.

The use of unmodified silica as a resin additive was investigated. Comparing the silica and hybrid blends may elucidate the effects of the organic component of the hybrids on the resin. However, it must be noted that the size and shape of the silica particles and the hybrids differed, so a direct comparison was not possible, as morphology of the additive is likely to affect the resin properties.
5.2 Results and discussion

5.2.1 Epoxy resin

Silica nanoparticles of diameter 20 nm [1] and the organic-inorganic hybrids synthesised in chapter 4 have been blended with the resin XLVR16-2, supplied by ACG (chapter 2 section 2.3). This resin system consists of the trifunctional epoxy resin TGPAP (5.1) (XLVR16-2R) and an anhydride curing agent, 1-methyl-5-norbornene-2,3-dicarboxylic anhydride (5.2) (XLVR16-2H).

(5.1): TGPAP

(5.2): Methyl-5-norbornene-2,3-dicarboxylic anhydride

5.2.2 Silica nanoparticles

5.2.2.1 Blending with the epoxy resin

The use of commercial silica particles of diameter 20 nm as resin additives was investigated. Nano-sized particles were chosen in order to maximise the area of
interaction between the resin and additive as this may lead to the greatest enhancement in thermal properties [5-9]. SEM of the hybrids synthesised in chapter 4 showed, following dispersion in acetone, that they consisted of particles of less than 100 nm diameter. Using silica particles of the same order of magnitude would allow a more direct comparison of the resin blends than less well-matched sizes. However, silica particles of diameter 100 nm were available commercially only as a suspension in ethylene glycol, which would be difficult to remove completely from the resin blends owing to its high boiling point.

Silica was added at a concentration of 5 phr; this equates to 2.2 weight %. The particles were pre-mixed with the anhydride, XLVR16-2H, before addition of the epoxy, XLVR16-2R. The blends appeared well-mixed both before and after cure, with no agglomerates of the additive visible, suggesting that the silica particles were well-dispersed.

5.2.2.2 DMTA

DMTA of the cured blends was carried out. The cure schedule recommended by the manufacturer involved a 60 °C initial cure, followed by a 175 °C post cure.

XLVR16-2 has a long gel time (approximately 10 hours at 60 °C) and as such, silica has a large window of opportunity in which to sediment from the resin. Therefore, the initial cure temperature was increased from 60 °C to 150 °C in order to reduce the gel time. Curing XLVR16-2 at 150 °C gave a gel time of 10 minutes. Conversely, increasing the cure temperature would also reduce the viscosity of the resin and so increase the mobility of the silica particles, favouring their agglomeration. Silica was not observed to sediment from the resin at either cure temperature. The post-cure temperature was increased from 175 °C to 200 °C to elucidate its effect on $T_g$. It was anticipated that increasing the post-cure temperature might increase the degree of cross-linking and so increase the $T_g$ of the resin. Too high a post-cure temperature would lead to the thermal decomposition of the resin.

The effect of curing temperature on the $T_g$ of the blends was investigated (table 5.1, figures 5.1 and 5.2). The $T_g$s of the resin with and without the inclusion of silica were compared (table 5.1).

It can be seen (figures 5.1 and 5.2) that the effect of cure schedule on $T_g$ was much greater in the case of the silica-modified resin than the unmodified resin. The
unmodified resin showed no significant difference in $T_g$ between a 60 °C and 150 °C initial cure. However, a slightly higher $T_g$ was observed in each case when the higher post curing temperature was employed. It is assumed that the higher post-cure temperature increases the cross-link density, and hence $T_g$, of the resin.

<table>
<thead>
<tr>
<th>Cure temperature (°C)</th>
<th>Post-cure temperature (°C)</th>
<th>Mean $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No silica</td>
<td>5 phr silica</td>
</tr>
<tr>
<td>60</td>
<td>175</td>
<td>189.7</td>
</tr>
<tr>
<td>60</td>
<td>200</td>
<td>192.2</td>
</tr>
<tr>
<td>150</td>
<td>175</td>
<td>189.0</td>
</tr>
<tr>
<td>150</td>
<td>200</td>
<td>191.4</td>
</tr>
</tbody>
</table>

Table 5.1: $T_g$ of XLVR16-2 unmodified and blended with 5 phr 20 nm silica

Figure 5.1: Peak in tan $\delta$ from DMTA thermogram of XLVR16-2 with no silica added
Chapter 5: Silica and organic-inorganic hybrids as resin additives

Figure 5.2: Peak in tan δ from DMTA thermogram of XLVR16-2 with 5 phr silica added

The $T_g$ of the resin samples to which silica was added showed a greater dependence on cure temperature than the unmodified resin (table 5.1). In the case of a 60 °C cure the $T_g$ was slightly increased by the addition of silica, while the samples cured at 150 °C showed a reduction in $T_g$ on the addition of silica. This observation may be due to a difference in the morphology of the samples cured at different temperatures. A higher initial cure temperature would lead to a reduction in viscosity and so greater mobility of the silica particles within the resin. Hence, it would be likely to favour their agglomeration. This theory concurred with the observation that a lower cure temperature yielded a higher $T_g$. If the additive was very well dispersed it would have a large surface area in contact with the resin; hence, it would be constrained by the resin to a greater extent than an agglomerated system. This constraint may lead to a decrease in the mobility of the organic polymer chain resin and hence an increase in the observed $T_g$.

The shape of the peak in tan δ varied with the initial cure temperature in the same manner for samples both with and without the incorporation of silica (figures 5.1 and 5.2). A 60 °C cure yielded a higher, narrower peak in tan δ than an initial 150 °C cure. A lower peak in tan δ corresponds to fewer degrees of freedom in the material, i.e. a higher degree of cure [10]. A higher initial cure temperature might be expected to yield a more highly cross-linked product, as suggested by the DMTA thermogram.
in this case. A broad peak in tan δ is due to the presence of many species, leading to smearing of the glass transition. This suggested that a greater number of species were formed when the resin was cured at 150 °C than at 60 °C. The epoxy-anhydride reaction is complex and involves several competing processes (figures 5.3 to 5.5) [11]. The relative rates of these reactions will vary with temperature. Thus the nature of the products formed will depend on the cure temperature, as observed in this case by the variation in the shape of the peak in tan δ with cure temperature.

**Figure 5.3:** Opening of anhydride ring with a hydroxyl group to form a monoester

**Figure 5.4:** The carboxylic acid group of the opened anhydride reacts with an epoxy group to give an ester linkage
5.2.2.3 TG analysis

TG analysis of the resin cured at 150 °C was carried out. It can be seen (figures 5.6 and 5.7) that the incorporation of silica at 5 phr had little effect on the thermal degradation of the resin; the onset temperature and rate of degradation were nearly identical for both post-cure temperatures. In each case the residual mass at 1000 °C was greater with silica present than without, owing to the high thermal stability of silica, which does not degrade at this temperature. The residual mass at 1000 °C was approximately 5 % higher in each case. This was greater than the mass of silica added to the resin (5 phr, 2.2 weight %). Therefore, the presence of silica had modified the degradation pathway perhaps constraining the resin around it or promoting the formation of thermally stable silicon oxycarbide species [12, 13].
Figure 5.6: TG thermogram of XLVR16-2 cured at 150 °C and post cured at 175 °C

Figure 5.7: TG thermogram of XLVR16-2 cured at 150 °C and post cured at 200 °C

The small silica particles were unlikely to be fully condensed owing to steric constraints and so could be expected to possess residual silanol functionality. These silanol groups would be able to react with the resin, opening either epoxy or anhydride rings. It may be this tethered, but partially degraded, organic material that
remained after excursion to high temperature. From figures 5.6 and 5.7 it may be
deduced that in some way the silica is inhibiting the degradation of the organic
material between approximately 700 and 1000 °C.

5.2.2.4 Morphology

SEM of the resin blends was carried out in order to reveal whether or not the
variation in thermal properties was related to a variation in morphology, perhaps
dependent on the initial cure temperature. However, no morphology difference was
observed between fracture surfaces of the modified and unmodified resins. Single-
phase fracture surfaces were revealed and the silica particles could not be seen.
Therefore, no difference in morphology between the resins cured at different
temperatures was observed. It is likely that this was due to the low concentration of
silica present. The rigid nature of the silica additive is unlikely to lead to stress
concentrations around the particles [14] and so fracture would be more likely to
occur in the bulk resin rather than at resin-additive interfaces (of which there are
statistically few).

5.2.2.5 Fracture toughness

The effect of the addition of 5 phr silica on the fracture toughness of XLVR16-2 was
evaluated using compact tension specimens. It can be seen in figure 5.8 that the
fracture toughness of XLVR16-2 was not significantly increased by the addition of
silica.

![Fracture toughness of XLVR16-2 with the addition of 5 phr silica](image)

**Figure 5.8:** Fracture toughness of XLVR16-2 with the addition of 5 phr silica
5.2.3 Sol-gel hybrids

5.2.3.1 Blending with the epoxy resin

The use of the hybrid particles synthesised in chapter 4 as resin additives was investigated. The particles were capped with methoxytrimethylsilane, added at two-thirds of the molar concentration of TEOS and dried at pH 2. SEM of the hybrids showed that, after dispersion in acetone, they consisted of particles of less than 100 nm diameter (chapter 4 section 2.8.1).

The hybrid particles were added to the resin at a concentration of 5 phr. The particles were pre-mixed with the anhydride, XLVR16-2H, to disperse them before addition of the resin. The blends appeared well-mixed but the additives phase-separated during cure to form a layer at the bottom of the samples. XLVR16-2 is a low viscosity resin with a long gel time. The use of a higher viscosity resin system with a shorter gel time might prevent sedimentation of the hybrid.

5.2.3.2 DMTA

DMTA of the cured blends was carried out. Samples were cured at 60 °C followed by a post cure at 175 °C, as recommended by the resin manufacturer. DMTA thermograms of the resin with and without the inclusion of the additive are shown in figure 5.9.

It can be seen in figure 5.9 that the addition of the hybrid to XLVR16-2 at a concentration of 5 phr caused a reduction in Tg of 5 °C. This may be due to a degree of plasticisation caused by the presence of the hybrid particles. These particles could sterically disrupt the epoxy network and lead to a reduction in the degree of cross-linking.

In the case of the addition of 5 phr silica to XLVR16-2 an increase in Tg of 5 °C was observed after curing at 60 °C and a 175 °C post-cure (table 5.1). This difference between the thermal properties of the silica blend and the hybrid blend may be due to the slightly smaller size of the silica particles. The silica particles may have sterically hindered the cross-linking reaction to a lesser extent than the hybrid particles.
Figure 5.9: DMTA thermogram of XLVR16-2 blended with 5 phr hybrid

The interaction of the particles with the resin might also affect the $T_g$ of the blends. The silica particles, owing to steric constraints caused by their nanoscopic size, would not be fully condensed. The residual silanol groups at the surface of the silica particles would be able to react with the resin components (for example as in figure 5.3). The hybrid particles were capped with methoxytrimethyisilane and would be expected to exhibit a low degree of surface functionality. Therefore, they would be able to undergo little or no reaction with the resin. Bonds between the particles and matrix resin might counteract plasticisation caused by the particles disrupting the cross-linked network.

5.2.3.3 TG analysis

TG analysis of the hybrid blend was compared to that of unmodified XLVR16-2. It can be seen that the incorporation of the hybrid at 5 phr had only small effects on the onset and rate of degradation of the resin (figure 5.10).
Surprisingly, the residual mass at 1000 °C was smaller with the hybrid present than without. This contrasted with TG analysis of the silica blends (figures 5.6 and 5.7), in which case the presence of silica increased the residual mass. The onset of decomposition of the hybrid blends was reduced by approximately 15 K with respect to XLVR16-2. The reduction in the onset of degradation and residual mass above 750 °C may be due to the hypothesised plasticisation caused by the presence of the hybrid particles. This agreed with the DMTA data, which also suggested that the thermal properties of the hybrid blends were reduced with respect to the silica blends.

### 5.2.3.4 Morphology

The hybrid particles were easily dispersed in the resin on mixing. However, during cure the additive sedimented to form a hybrid-rich layer at the bottom of the sample. The low viscosity and long gel time of XLVR16-2 gave the additive a large window of opportunity in which to agglomerate. It is likely that the hybrid particles were unable to form covalent bonds with the resin to a significant degree and so would not become tethered to the resin; the blend would be purely a physical one. This contrasted with the silica particles, which did not significantly agglomerate in the resin and had the potential to bond to it.
5.2.3.5 Fracture toughness

The effect of the addition of 5 phr of the hybrid particles on the fracture toughness of XLVR16-2 was evaluated using compact tension specimens. It can be seen in figure 5.11 that the fracture toughness of XLVR16-2 was decreased by approximately 25% on addition of the additive. This contrasted with the addition of silica particles to XLVR16-2, which had no significant effect on the fracture toughness of the resin (figure 5.8). As noted in section 2.3.4 the hybrid blends were not homogeneous. It is likely that blend morphology would affect fracture toughness and so a well-dispersed hybrid additive might give a different value of $K_{1c}$.

![Fracture toughness of XLVR16-2 with and without 5 phr hybrid](image)

*Figure 5.11: Fracture toughness of XLVR16-2 with and without 5 phr hybrid*

5.3 Conclusions

Silica particles of radius 20 nm and hybrid particles, as synthesised in chapter 4, were blended with the low viscosity epoxy-anhydride resin system, XLVR16-2. The particles were added to the resin at a concentration of 5 phr. The cured blends were characterised in terms of their thermal properties and fracture toughness.

Comparison of the properties of the silica and hybrid blends cannot simply reveal the effect of the organic component. The structure, morphology and surface
functionality of the particles differed. The surface functionality affects interaction with the resin and hence the properties of the blend. The hybrid particles were coated with methoxytrimethylsilane and as such were largely unable to react with the resin components.

The silica particles employed were very small (20 nm diameter) and were unlikely to be fully condensed owing to steric constraints. Therefore, they were likely to have silanol functionality at their surface. Silanol groups would be able to participate in the epoxy-anhydride reaction, by opening either the epoxy or anhydride ring (figures 5.3 and 5.12). In this way the silica particles could become physically bonded to the matrix resin.

The hybrid particles would not be able to bond so easily to the resin. Surface analysis (XPS) of the material would reveal to what extent it was methyl functionalised. The different manner in which the hybrid and silica particles interact with the resin would, in part, explain their different effects on its properties. The hybrid particles slightly reduced the thermal stability of XLVR16-2. This is likely to have been due to plasticisation, the hybrid particles interfering with the incipient cross-linked network during cure. The individual hybrid particles were not well resolved by SEM (chapter 4 figure 4.18) but appear to be approximately 100 nm in diameter. Therefore, these particles were larger than the silica particles employed and so would have a greater steric effect on the cross-linking of the matrix resin.

The thermal properties of the silica blends were shown to vary with the cure and post-cure temperatures employed. It was hypothesised that this was due to variation in blend morphology. It is possible that a higher temperature initial cure resulted in greater agglomeration of the additive because of the reduced viscosity of the resin and hence increased mobility of the additive. An agglomerated product would be more likely to interfere with the cross-linked network and so cause plasticisation.
SEM of the silica blends failed to elucidate their morphology. The particles were present at a low concentration (5 phr, 2.2 weight %) and were not observed on the fracture surfaces.

The presence of silica had no significant effect on the fracture toughness of the resin. However, the hybrid particles reduced the fracture toughness by approximately 25%. This result contradicted the hypothesis of plasticisation in these blends implied by DMTA and TG analysis. Plasticisation of the matrix resin would be expected to reduce its cross-link density and so increase its fracture toughness. This anomalous result may be attributable to the difference in morphology of the samples. The hybrid phase separated in the fracture toughness specimens but appeared well-dispersed in the thinner DMTA and TG analysis samples.

Silica is a brittle material [15] and so would not be expected to toughen the resin. It was hoped that the addition of an organic phase (i.e., the hybrid particles) would counteract the brittle nature of the inorganic phase and so maintain or enhance the fracture toughness of the matrix resin. However, the addition of silica particles to the resin at 5 phr was observed not to have an embrittling effect. It has been demonstrated that Boltorn E1 does not toughen XLVR16-2 when added at concentrations of 5, 10 or 20 phr (chapter 2). It may be that the use of an alternative organic phase, for example a thermoplastic HBP, at the core of the particles would be more effective at toughening the resin.

The hybrid particles sedimented to form a layer at the bottom of the resin during cure. If smaller particles could be synthesised they may remain better dispersed. In addition, the potential to form covalent bonds with the resin, as in the case of the silica particles, may aid in the maintenance of a fine dispersion during cure. However, it was shown that when the particles were not capped with methoxytrimethylsilane they agglomerated to a greater degree (chapter 4).

XLVR16-2 was chosen as the matrix resin because of its potential for use in low-cost manufacturing techniques, such as RTM. It is a low viscosity resin with a long gel time. If a resin with a higher viscosity or a shorter gel time was used it might inhibit sedimentation of the hybrid particles during cure. Unfortunately, these potential improvements could not be studied owing to lack of time.
5.4 Experimental

5.4.1 Instrumentation

Bending DMTA was performed using a Polymer Laboratories Mark II Dynamic Mechanical Thermal Analyser. DMTA was carried out in single cantilever mode at a frequency of 1 Hz, strain x4, and with a ramp rate of 2 K.min\(^{-1}\). TG analysis was performed in a nitrogen atmosphere using a Perkin-Elmer TGA7 Thermogravimetric Analyzer, at a ramp rate of 10 K.min\(^{-1}\).

SEM of gold-coated fracture surfaces was carried out using a LEO 1550 Field Emission Scanning Electron Microscope.

Gel time measurements were performed on a Rheometric Scientific ARES (Advanced Rheometric Expansion System) at 1 Hz between 50 mm diameter parallel plates and at temperatures in accordance with the cure cycle of the resin.

Fracture toughness testing was carried out in accordance with ASTM D 5045-99, using compact tension specimens. The sawn-in crack and holes were machined. The natural crack was generated using a fresh razor blade for each contact with the resin. Specimens were tested using an Instron 5500R tensometer with a 10 kN load cell and a crosshead displacement rate of 2 mm.min\(^{-1}\) at ambient temperature (20 to 22 °C).

5.4.2 Materials

The resin XLVR16-2 was obtained from ACG. The 20 nm diameter silica particles, Nyacol® Nyasil 20, were supplied by Nyacol® Nano Technologies. All other chemicals were obtained from Aldrich and were used as received. The hybrid particles were synthesised as in chapter 4 section 4.8.2, using the middle concentration of methoxytrimethysilane.
5.4.3 XLVR16-2

XLVR16-2H (12.5 g) was mixed with XLVR16-2R (10 g) at 2700 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The material was cast into an aluminium mould that had been sprayed with a silicone release agent and then degassed in a vacuum dessicator. The specimens were cured for 4 hours at 150 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C or 200 °C and allowed to dwell at this temperature for 120 minutes. Alternatively, the specimens were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C or 200 °C and allowed to dwell at this temperature for 120 minutes. After cooling to ambient temperature the samples were demoulded. DMTA samples were polished to size (approximately 25 x 10 x 2 mm\(^3\)). The blends were also cured in the rheometer at 10 % strain in order to determine the gel time.

Compact tension specimens (approximately 48 x 50 x 15 mm\(^3\)) were cast in a mild steel mould lined with teflon release paper and degassed in a vacuum oven. They were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C and allowed to dwell at this temperature for 120 minutes before being allowed to cool to ambient temperature.

5.4.4 Silica nanoparticles

Nyacol® Nyasil 20 (1.0 g) was mixed with XLVR16-2H (12.5 g) by hand using a spatula until the silica appeared to be evenly dispersed. XLVR16-2R (10 g) was added and the blend mixed at 2700 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The material was cast into an aluminium mould that had been sprayed with a silicone release agent and then degassed in a vacuum dessicator. The specimens were cured for 4 hours at 150 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C or 200 °C and allowed to dwell at this temperature for 120 minutes. Alternatively, the specimens were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C or 200 °C and allowed to dwell at this temperature for 120 minutes. After cooling to ambient temperature the samples were demoulded. DMTA samples were polished to size (approximately 25 x 10 x 2 mm\(^3\)).

Compact tension specimens (approximately 48 x 50 x 15 mm\(^3\)) were cast in a mild steel mould lined with teflon release paper and degassed in a vacuum oven. They
were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C and allowed to dwell at this temperature for 120 minutes before being allowed to cool to ambient temperature.

### 5.4.5 Hybrid particles

Hybrid particles (1.0 g) were mixed with XLVR16-2H (12.5 g) by hand using a spatula until the silica appeared to be evenly dispersed. XLVR16-2R (10 g) was added and the blend mixed at 2700 rpm for 40 seconds in a Hauschild Speed Mixer™ DAC 150 FV centrifugal mixer. The material was cast into an aluminium mould that had been sprayed with a silicone release agent and then degassed in a vacuum dessicator. The specimens were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C and allowed to dwell at this temperature for 120 minutes. After cooling to ambient temperature the samples were demoulded. DMTA samples were polished to size (approximately 25 x 10 x 2 mm\(^3\)).

Compact tension specimens (approximately 48 x 50 x 15 mm\(^3\)) were cast in a mild steel mould lined with teflon release paper and degassed in a vacuum oven. They were cured for 24 hours at 60 °C, then heated at 20 K.hour\(^{-1}\) to 175 °C and allowed to dwell at this temperature for 120 minutes before being allowed to cool to ambient temperature.

### 5.5 References


Chapter 6: Conclusions and future work
6.1 Introduction

The ultimate objective of the project was the development of a polymer matrix for structural composites, having enhanced thermal and mechanical properties compared to current systems, whilst maintaining easy processability.

In the pursuit of this objective, an investigation into the potential of the HBP Boltorn E1 [1] as a resin additive was carried out. Literature studies suggested this material had the potential to act as both a toughening agent and rheology modifier to a matrix resin [2]. The synthesis of sol-gel hybrid particles was also investigated, as it was hypothesised that the incorporation of inorganic material into an organic matrix may enhance its thermal stability [3] and that this benefit may be greatest in a nano-scale hybrid [4, 5].

6.2 Boltorn E1

6.2.1 Conclusions

The use of the HBP Boltorn E1 as a resin additive was investigated. Boltorn E1 was blended with various tetrafunctional, trifunctional and difunctional epoxy resins at concentrations of 5, 10 and 20 phr. The resin blends were characterised in terms of their thermal, rheological and mechanical properties. It was hoped that the addition of Boltorn E1 to the resins would increase their fracture toughness whilst enhancing or maintaining their processability. However, it was shown that whilst having a negligible impact on processability, Boltorn E1 failed to increase the fracture toughness of the blends.

Boltorn E1 initially formed a homogeneous blend with all of the resins investigated. SEM revealed that a two-phase morphology was developed during cure for all of the blends except DGEBA/piperidine, which was single-phase. During polymerisation Boltorn E1 became insoluble in the growing network, owing to the changing solubility parameters of the polymer chains and so formed a secondary phase. It has been shown that in general a two-phase morphology is required in order for a toughening effect to be observed [6].
Structural components for aerospace applications must be able to withstand high temperatures for thousands of flying hours. TG analysis of the resin blends with Boltorn E1 showed that it did not significantly reduce their thermal stability. DMTA of the resin blends showed that the addition of Boltorn E1 at a concentration up to 20 phr did not reduce the $T_g$ of the phase-separated blends by more than a few degrees centigrade. Therefore, the addition of Boltorn E1 to the resins tested should not significantly impair their thermal properties.

The decrease in $T_g$ caused by the addition of Boltorn E1 varied with the matrix resin employed. The blends displayed a correlation between morphology and degree of plasticisation. The least phase-separated systems showed the greatest decrease in $T_g$ on addition of Boltorn E1, owing to plasticisation caused by phase mixing. The high epoxy equivalent weight of Boltorn E1 [1] with respect to the resins caused a reduction in the cross-link density.

Boltorn E1 had a negligible effect on the viscosity of the resins that were more viscous than, or of comparable viscosity to, the additive. Boltorn E1 is more viscous than XLVR16-2 and XLVR15-2 and as such slightly increased the viscosity of these blends. However, these increases were not great and the processing windows of the resins were not significantly affected by the addition of Boltorn E1. XLVR15-2 and XLVR16-2 are low viscosity resin systems, suitable for use in resin infusion techniques such as RTM. The addition of Boltorn E1 to these resins would not inhibit its use in such low cost manufacturing techniques.

The use of Boltorn additives (both thermoplastics and thermosets) as toughening agents to epoxy resins has been reported in the literature [2, 7, 8]. Toughness enhancements were reported for difunctional, trifunctional and tetrafunctional resins.

An increase in the $K_{IC}$ value of DGEBA on addition of Boltorn E1 has been reported (with the curing agent isophorone diamine) [2]. An increase of approximately 50 % was observed on addition of 5 phr of the additive and nearly 100 % with 20 phr of Boltorn E1. The additive toughened the resin by cavitation and plasticisation, the same mechanism as conventional rubber toughening agents such as CTBN [9]. Therefore, the thermoset Boltorn E1 is likely to be most suitable for toughening low-functionality resins. The major advantage of the use of Boltorn E1 over CTBN is that, at a concentration of 20 phr, the initial viscosity of the blend was an order of magnitude lower than that of a blend with the same concentration of CTBN [2, 9].
this work an increase in the toughness of the DGEBA systems was not observed. It is possible that changing the curing agent from piperidine or Jeffamine D230 to isophorone diamine would result in a toughening effect. The interaction between the additive and curing agent will affect the morphology of the blend and hence influence the toughness of the blends.

6.2.2 Future work

Thermoplastics have been shown to toughen highly cross-linked epoxy resins owing to their ability to allow a greater degree of shear yielding than cross-linked toughening agents can [10]. A thermoplastic Boltorn additive has been shown to successfully toughen a trifunctional epoxy when present as a co-continuous phase [8]. Therefore, the addition of a thermoplastic HBP or dendrimer to high performance resins should be investigated.

Linear thermoplastic toughening agents cause a dramatic increase in the resin viscosity and so significantly impair resin processability. Dendrimers and HBPs have lower viscosities than their linear analogues [11]. Therefore, thermoplastic dendrimers and HBPs have the potential to toughen highly cross-linked epoxy resins without causing the processability problems associated with conventional thermoplastic toughening agents. It would be interesting to evaluate the potential of hyperbranched analogues of conventional thermoplastic toughening agents, such as PES.

Boltorn E1 was added to the resins investigated at concentrations of up to 20 phr and, at these concentrations, did not increase the fracture toughness. It has been reported that in order to give a significant increase in impact strength a high concentration of a thermoplastic Boltorn additive, approaching a co-continuous morphology, must be used [7, 8]. Also, in order for conventional thermoplastic toughening agents to be effective a co-continuous morphology is required [10]. Therefore, in addition to investigating the use of a thermoplastic additive, increasing its concentration to a value that yields a co-continuous morphology should be attempted. In this way, the fracture toughness of the matrix resin might be enhanced. However, the more compact nature of the HBP than conventional linear thermoplastic toughening agents might affect the formation of a co-continuous network.
The values of $K_{1c}$ achieved for the difunctional systems were higher than those reported in the literature for the unmodified resin [2, 9]. In order to give the limiting minimum value of fracture toughness, as required for the determination of $K_{1c}$ [12], the crack generated in the compact tension samples must be a very sharp natural crack. It is possible that the cracks, formed by pressing a razor blade into the specimen, were not sufficiently sharp to give a true value of $K_{1c}$. Repetition of the fracture toughness tests for these systems should be carried out, ensuring a sharp, natural crack is generated. It is possible that in this case, the relative values of fracture toughness of the modified and unmodified resins might be altered.

Whilst the majority of the resin blends with Boltorn E1 were two-phase, the DGEBA/piperidine blends were homogeneous. In order to predict the morphology of the resin blends with an additive, the solubility parameters of the species present must be calculated [13-15]. It is not sufficient to compare the solubility parameters of the starting materials as in many cases the blends are initially homogeneous and the two-phase morphology is induced during cure [13-15]. During the polymerisation process a large number of different oligomers are formed as the species present react and chain extension occurs. Therefore, predicting the solubility parameters of the oligomers in the reaction mixture is very complex. In order to predict the morphology of a resin blend with a potential toughening agent computer modelling should be carried out.

6.3 Sol-gel hybrids

6.3.1 Conclusions

Nano-scale hybrids of Boltorn E1 and silica have been successfully synthesised by two sol-gel methods. The nano-scale nature of the materials was confirmed by microscopy studies.

6.3.1.1 Conventional sol-gel synthesis

The first method employed in hybrid synthesis was a conventional sol-gel technique. The inorganic precursor (TEOS or TMOS) was added to a solution of Boltorn E1 and the hydrolysis of the alkoxy silane and condensation of silica was carried out in situ. It was hoped that silica condensation would occur around the organic polymer and
an individual shell would coat each HBP molecule [16]. However, a degree of aggregation of the organic phase occurred; microscopy studies revealed the domain sizes to be of the order of 50 nm whilst a Boltorn E1 molecule has diameter 3.2 nm. Therefore, it can be inferred that whilst a nano-scale hybrid was formed, the organic and inorganic phases were not associated at a molecular level.

In order to be dispersed in a matrix resin the hybrid product should be particulate. In this case, a particulate product was formed on condensation of silica but during the drying process these particles agglomerated to form a monolith. A dilute solution of Boltorn E1 was taken as the starting point for the synthesis in order to physically separate the HBP molecules and encourage the formation of a particulate product. As silica condensation proceeded hybrid particles were observed to precipitate from the reaction mixture. The particles were dried by evaporation of the solvent. During this process the particles became closer together and so interparticular condensation occurred.

6.3.1.2 Emulsion method of hybrid synthesis

Owing to the lack of success in isolating nano-scale hybrid particles using the conventional sol-gel technique, an alternative method for their synthesis was investigated. In this case, an emulsion of Boltorn E1 was employed as the starting point for the hybrid synthesis. An alkoxysilane was added to the emulsion and its hydrolysis and the subsequent condensation of silica were carried out using a basic catalyst.

A particulate organic-inorganic hybrid was successfully synthesised using this method. The hybrid nature of the particles was confirmed by IR spectroscopy. Electron microscopy showed that, whilst particles of less than 100 nm had been successfully formed, the particles displayed a degree of agglomeration.

Particle agglomeration was reduced by the addition of a capping agent to the hybrid sol. The capping agent was able to react with the residual silanol and alkoxysilane groups at the surface of the hybrid particles. This material showed only a small degree of particle agglomeration, the aggregates formed being sub-micron in size and individual particles approximately 100 nm in diameter.
The hybrid particles synthesised using the emulsion method were blended with the trifunctional epoxy resin XLVR16-2 at a concentration of 5 phr. The cured blends were characterised in terms of their thermal properties and fracture toughness.

The hybrid particles had been capped with methoxytrimethylsilane and so were expected to be predominantly methyl functionalised. Therefore, they would be largely unable to form covalent bonds with the resin components. The surface functionality affects the interaction of the particles with the resin and so will affect the properties of the cured blend.

The hybrid particles sedimented during cure to form a layer at the bottom of the resin. If smaller particles could be synthesised or if the particles could be tethered to the resin by covalent bonds they might remain better dispersed. However, it was shown that when the hybrid particles were not capped, and so would be more easily able to form covalent bonds with the resin, they agglomerated to a greater degree. XLVR16-2 is a low viscosity resin with a long gel time. A resin with a higher viscosity or a shorter gel time might inhibit sedimentation of the hybrid particles.

The hybrid particles slightly reduced the thermal stability of XLVR16-2. It was assumed that this was due to plasticisation, the hybrid particles sterically interfering with the incipient cross-linked resin matrix. However, the hybrid particles reduced the fracture toughness of the resin by approximately 25 %. This result contradicted the hypothesis of plasticisation inferred from DMTA and TG analysis. Plasticisation of the matrix resin would be expected to reduce its cross-link density and so increase its fracture toughness. Therefore, it is likely that the particles acted as crack initiators rather than crack arrestors.

### 6.3.2 Future work

#### 6.3.2.1 Conventional sol-gel synthesis

The hybrids synthesised using this method displayed nano-scale phase interaction. However, the material formed was not particulate in nature. Future work should investigate isolation of the particulate sol formed prior to removal of solvent, whilst preventing agglomeration of the particles and of Boltron E1.
Boltorn E1 was dried by azeotropic distillation in toluene solution prior to reaction with the coupling agent. Drying is necessary because the presence of water would cause hydrolysis of the isocyanate functionalised coupling agent. Cross-linking of the HBP epoxy rings could be auto-catalysed by the hydroxyl groups, situated at the periphery of the core of Boltorn E1. The high temperatures involved in azeotropic distillation would promote homopolymerisation. Therefore, the use of an alternative, ambient temperature drying method, such as vacuum drying, should be investigated in order to prevent chemical aggregation of Boltorn E1.

The tertiary amine, DBU, used as a catalyst in the reaction of Boltorn E1 with the coupling agent 3-(triethoxysilyl)propyl isocyanate, was able to catalyse cross-linking of the epoxy groups of the HBP. Therefore, its use promoted the aggregation of the organic phase. The presence of a coupling agent was required to prevent gross phase separation of the organic and inorganic components. The use of a coupling agent that does not cause cross-linking of the epoxy groups may reduce the degree of agglomeration of Boltorn E1. The use of such coupling agents, for example GPTMS or (3-mercaptopropyl)trimethoxysilane, should be investigated.

Prior to drying the reaction mixture, a particulate product was observed. However, during the drying process these particles agglomerated to yield a monolith. In order to determine the morphology of the particles formed, electron microscopy of the product prior to drying should be carried out. If nano-scale particles were observed alternative methods of isolating them should be investigated. The drying technique used in the case of the emulsion method of hybrid synthesis could be employed. In this case, excess water was added to the reaction mixture and it was allowed to dry at ambient temperature and pressure [17]. Alternative methods of product isolation, such as centrifugation, filtration or freeze-drying could be investigated in order to preserve the particulate nature of the product.

6.3.2.2 Emulsion method of hybrid synthesis

The hybrid particles synthesised using this method were of approximate diameter 100 nm and were shown by SEM to agglomerate only to a slight extent. However, these particles were observed to sediment when blended with the epoxy resin XLVR16-2. This sedimentation might be reduced by a reduction in the size and agglomeration of the particles. Therefore, future work should concentrate on these aims, possibly in conjunction with the use of a thermoplastic HBP.
It was assumed that the hybrid particles had a core-shell structure, with Boltorn E1 at their centre surrounded by silica. Direct evidence for this morphology has not yet been obtained. It may be possible to visualise the internal structure of the particles by SEM if they could be freeze fractured. However, this would only reveal morphology, the chemical nature of the phases observed would not be known.

Indirect confirmation of the two-phase nature of the particles may come from surface analysis. If the surface of the particles could be shown to consist of silica it may be inferred that Boltorn E1 was sequestered at the centre of the particles, as IR spectroscopy confirmed the presence of both phases. The particle surfaces could be characterised by XPS.

It was hoped that the droplets of Boltorn E1 would act as nucleation sites for the deposition of silica. However, it is possible that self-nucleation would occur, leading to the formation of inorganic silica particles that do not have a Boltorn E1 core. The density of silica is 2.2 g.cm$^{-3}$, whilst that of Boltorn E1 is 1.04 g.cm$^{-3}$. Therefore, the silica particles will be more dense than the hybrid particles and so, in theory, could be separated from the hybrid product by differential centrifugal sedimentation [18].

A monofunctional capping agent, methoxytrimethylsilane was added to the hybrid sol prior to isolation. Therefore, it was anticipated that the majority of the particle surfaces possessed methyl functionality. It is not known what fraction of the particle surfaces are methyl functionalised. Again, XPS may be used to determine the surface functionality.

The capping agent added was monofunctional with respect to alkoxysilane groups. The methyl groups of methoxytrimethylsilane may sterically hinder its reaction with the hybrid particles. Therefore, the effect of adding a difunctional capping agent, such as dimethoxydimethylsilane, should be investigated. A higher proportion of the surface of this molecule is methoxy functionalised and so it may be more easily able to react with the hybrid particle, in terms of steric hindrance, than methoxytrimethylsilane.

Agglomeration and interparticular condensation may be further prevented by the addition of surfactant to the hybrid sol after the capping agent. A surfactant might stabilise the particulate dispersion. After isolation of the hybrid particles the surfactant must be removed by washing with water. The presence of the surfactant
on blending the particles with a resin could cause plasticisation of the resin and so impair its thermal properties [19].

The thermoset Boltorn E1 did not toughen XLVR16-2 when added at concentrations up to 20 phr. It may be that the use of an alternative organic phase, for example a thermoplastic HBP, at the core of the particles would be more effective at toughening the resin. Therefore, the use of such an agent as the organic phase of a hybrid particle should be investigated. In this way, it might be possible to combine a toughening effect imparted by the organic phase with an increase in thermal stability imparted by the inorganic phase on the resin.

6.3.2.3 Non-hydrolytic method of hybrid synthesis

Non-hydrolytic sol-gel techniques could provide an alternative route to the synthesis of hybrid nano-particles. An advantage of this method is that it is carried out under non-aqueous conditions, so the incorporation of water into a matrix resin on blending with the hybrid would be avoided. This is an important consideration because of the catastrophic effect of water on the thermal properties of epoxy resins [19].

The non-hydrolytic method could involve the reaction of a silicon halide with an oxygen donor to yield inorganic silica (figure 6.1) [20] in the presence of Boltorn E1. The reaction involves the co-ordination of the oxygen atom to the silicon halide (via the silicon atom), followed by cleavage of the O-R bond of the oxygen donor. The oxygen donor may be, for example, an alkoxide, alcohol, ether, aldehyde or ester. This method would, as in the hydrolytic sol-gel case, involve the condensation of silica around Boltorn E1, which could be present in dispersion or solution.

![Figure 6.1: Non-hydrolytic route to inorganic oxides][20]

\[ \text{Exchange} \]

\[ \text{M-O-R} + \text{Si-X} \rightarrow \text{M-O-Si-X} \]

\[ \text{R-X} \]

\[ \text{M-X} \]

\[ + \text{Si-OR} \]
These reactions are typically carried out in an inert atmosphere using a Lewis acid catalyst (often iron(III) chloride) and at a temperature of 85-110 °C. Under these conditions inorganic silica will be formed and it is hoped that it will grow using the Boltorn E1 molecules as nuclei.

A potential difficulty in the use of the non-hydrolytic sol-gel method could be the presence of the epoxy groups on Boltorn E1. These groups may be able to act as oxygen donors themselves and so lead to side reactions. Equally, the hydroxyl groups present on thermoplastic Boltorn additives could act as oxygen donors.

A non-hydrolytic system could make use of the reaction of RSiCl₃ with EtSi(OEt)₃ in the presence of the organic phase. The use of EtSi(OEt)₃ may give more compatibility with Boltorn E1 than TEOS because of the ability of its ethyl group to form hydrophobic-hydrophobic interactions with the aliphatic shell of Boltorn E1. Competing factors over the choice of the R substituent exist. The longer the R group (for example hexyl) the more likely it would be that plasticisation of the matrix would occur. However, a short R group (e.g. methyl) would offer less of a compatibilising effect with the hydrophobic aliphatic chains of the HBP.

6.4 References
