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REVIEW

OLIGOMERIC AND POLYMERIC MODIFIERS FOR TOUGHENING OF EPOXY RESINS

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Abstract—The enhancement of properties of cured epoxy resins by the incorporation of modifiers into standard formulations is a subject that has received a great deal of attention over the last two decades. This paper presents an overview of the principles that have been explored to overcome the main deficiencies of epoxy resins, especially their brittleness, and reviews the scientific advances that have been made in this field. Particular attention is given to improvements in properties achieved by the addition of reactive oligomeric compounds, such as: (a) carboxyl and amino terminated butadiene–acrylonitrile, low molecular weight, statistical copolymers; (b) telechelic acrylate copolymers and terpolymers; (c) amine terminated polysiloxanes; and (d) chain extended carboxyl terminated perfluoro polyethers.

The use of functionalised thermally stable high molecular weight polymers, both rubbery and glassy, is also examined and their efficiency in enhancing the toughness of difunctional and multifunctional epoxy resins is considered. The polymers considered in greater detail are based on aromatic polyethers and polysiloxane elastomers, respectively.

INTRODUCTION

Cured epoxy resins are known to exhibit good engineering properties, such as high stiffness and strength, creep resistance and chemical resistance. In common with all thermoset plastics, however, they are intrinsically brittle. To alleviate this deficiency epoxy resins are frequently modified by dissolving in the liquid system a small proportion (10–20%) of a liquid rubber containing reactive end groups and allowing the precipitation of cross-linked rubbery particles during curing [1]. It is preferable that the modifying agent is a low molecular weight polymer to ensure that the viscosity of the resin is not increased excessively so that the processability of the system is not impaired [2].

An early theory to explain rubber toughening of brittle glassy polymers is due to Bucknall and Smith [3]. The basis of this theory is that rubber particles initiate the formation of crazes and control their growth [4]. Under tensile stress, crazes are formed at the points where the principal strain is maximum, i.e. near the equator of the rubber particles, and propagate outwards. The growth of crazes stops as a result of stress relaxations when they meet energy absorbing obstacles, such as smaller rubber particles, and prevents them to develop into large cracks. A high level of adhesion between the matrix and the rubber particles is necessary for the craze arresting mechanism to operate. A weakly adhering rubber particle would be pulled away from the matrix, leaving a hole which would intensify the stresses locally and induce fracture.

This mechanism is unlikely to operate, however, in the case of highly cross-linked systems since the chain length between cross-links is too short to effectively produce the fibrils of oriented chains acting as bridges between the two opposing surfaces of the craze [5].

More recent theories [6–8] for the toughening of highly cross-linked polymers by rubber inclusions involve the concept of shear yielding of the matrix around the particles as a mechanism for increasing the level of strain that the matrix will reach before fracture. Although the adhesion between matrix and rubber particles is a crucial factor in improving toughness by the shear yielding mechanism, it is the higher compliance of the particles relative to the matrix that is largely responsible for the onset of shear deformations in the matrix. Wu *et al.* [9] have put forward the concept of critical interparticle surface distance as a condition for inducing yielding in a matrix containing rubber particles. It is possible that the random distribution of particles in the matrix, together with an optimised packing arrangement of the particles, plays an important role in developing shear deformations within the matrix.

This mechanism, however, still relies on the ability of the matrix around the particles to undergo a certain extent of yielding and, therefore, it is unlikely that it will operate when the cross-linking density of the matrix is too high. For the latter case the only possibility to toughen the resin is by energy absorption through deformations within the rubber particle itself, particularly through crack bridging or volumetric dilations (e.g. microvoiding) [10].

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Obtaining a good bond between rubber particles and matrix is primarily a matter of "compatibility" and chemical reactions between the two phases. Full miscibility between a rubber and a resin does not produce effective toughening, but merely serves to plasticise the matrix. Total immiscibility is equally undesirable, since a completely immiscible rubber of reasonably high molecular weight, which would be required to achieve an adequate level of mechanical properties, will not form a fine dispersion in the resin due to inevitably large differences in viscosity between dispersed particles and matrix, nor will it produce a strong bond at the rubber–matrix interface. The ideal rubber for toughening purposes is one which is semi-miscible, i.e. the mixture is near the critical solution conditions around the cure temperature.

It is then possible to improve the adhesion between the epoxy matrix and the toughening phase by allowing the particle to precipitate from a homogeneous mixture so that they will contain not only the rubbery material but also the epoxy resin and possibly the catalyst to promote reactions between the two. Demixing via spinodal decomposition is important for designing the morphology of polymer blends, since the characteristic morphology can be fixed or frozen at various stages during the evolution of the phase separation process by quenching the demixed system below T_g. For thermosetting systems a spinodal decomposition induced by chemical reaction is even more effective than by thermal means [11]. It has been found that various reactive end groups in a liquid rubber modifier, e.g. carboxyl, hydroxyl, epoxy, mercaptan, phenol, methylol and amine, can be effective [12, 13] in inducing particle precipitation through reactions with an epoxy resin and to achieve a good interfacial bond.

Another weakness of conventional epoxy resins is their relatively large level of water absorption, which causes a large reduction in glass transition temperature [14, 15] and a deterioration in mechanical properties [16, 17]. The high affinity of epoxy resins towards water is explained by the presence of highly polar groups in the epoxy network. It has been proposed, in fact, that the diffusion of penetrant molecules into polymers depends on two factors [18], namely the forces of attraction between the polymer and the penetrant molecules, and the availability of appropriate molecular size holes in the polymer network. The first factor concerns the chemical nature of the penetrant in relation to that of the polymer. The relatively high water absorption capacity of epoxy resin derives from the presence of hydroxyl (OH) groups in the epoxy chains, which attract the polar water molecules through hydrogen-bond formation [19, 20]. The second factor, on the other hand, involves the presence of holes determined by the polymer structure and morphology, which in turn depends on the fluctuations in cross-link density, and molecular chain stiffness, hence their ability to closely pack in an amorphous system. The formation of an appropriate hole also depends on the cohesive energy density of the polymer and on the size of the penetrating molecules. Water molecules, for example, are hydrogen-bonded and can form clusters within the polymer [21]. Thus this particular factor-affecting diffusion is essentially a geometrical one, i.e. the free volumes available within the polymer for occupation by the penetrant molecules.

Although some attempts to reduce the water absorption of epoxy resins with low surface energy oligomers, such as siloxane and perfluoroether telechelic systems, have been made [22–25], the majority of workers have focused their attention on the synthesis of resins using highly fluorinated reactants [26–28]. The success of the latter is primarily due to a fairly even distribution of fluorine atoms within the network, which reduces the intrinsic rate of diffusion. The efficiency of modifiers, on the other hand, relies on their ability to form diffusion barriers consisting of co-continuous (interpenetrating) phases within the intrinsically hydrophilic matrix.

TOUGHENING OF EPOXY RESINS BY CTBN AND ATBN OLIGOMERS

McGarry and Willner [29] showed that low molecular weight carboxyl terminated butadiene–acrylonitrile copolymers (CTBN) are the most effective agents for improving the fracture toughness of epoxy resin. The CTBN used in epoxy resins has a molecular weight in the region of 2000–10,000, while the acrylonitrile content which allows the highest toughness of the resin is between 12 and 18 wt% [12]. It has been found that triphenylphosphine (TPP) is a very effective catalyst to promote the reaction between the carboxyl groups of the oligomer and epoxy groups of the resin [30], and it also assists the nucleation of the toughening rubber particles from the original solution.

Because of its relatively low viscosity the addition of CTBN does not impair appreciably the processability of the resin mixture.

By inducing the rubbery phase to precipitate the epoxy network remains essentially unchanged, thereby preserving its main properties [31], while the presence of fine precipitate rubbery particles [1–5 μm] imparts an enhanced resistance to crack propagation and impact strength [32]. The use of large amounts of CTBN, however, produces a simultaneous decrease in the glass transition temperature and modulus of the resin [33] through plasticisation effects. The choice of the modifier is determined by two factors. Firstly, there is a miscibility requirement, i.e. the oligomer must dissolve in the resin, but it has to precipitate before gelation. Secondly, there is a chemical requirement; i.e. the oligomer must react with the epoxide groups to achieve a high level of interfacial adhesion. Both requirements are met with the use of CTBN rubbers. The difference in solubility parameters between CTBN and DGEBA, for example, is sufficiently small to allow the oligomer to dissolve in the resin, but not so small that phase separation does not take place during curing. However, phase separation is governed by the reactions between the two before adding the hardener, which induces gelation of the resin by reacting first at the activated sites, i.e. the junctions between the epoxy groups and the acid groups of CTBN.

Studies performed on binary mixtures of bisphenol-A epoxy resin with either CTBN or ATBN (amine-terminated butadiene–acrylonitrile rubber) showed that these systems exhibit an upper critical solution temperature (UCST) phase behaviour [34, 35]. Mixtures of resin, telechelic oligomer and a curing agent, showing a single phase at the very early stage of curing, develop a two-phase structure via either a particle nucleation and growth (NG) or a spinodal decomposition (SD) as the cure process proceeds. During curing, in fact, the UCST is elevated by the increase in the molecular weight of the epoxy and hence the system is moved into a two-phase region. This implies that one can control the two-phase morphology by manipulating the kinetics of phase separation and curing reactions. It has been found that a high temperature cure (above 100°C) yields a dispersed-particle structure with fairly uniform particle size and that the particle size becomes smaller with increasing cure rate. Furthermore, a high temperature cure using a low reactivity curing agent produces spherical particles having a bimodal size distribution. On the other hand, a co-continuous two-phase structure is obtained with a low temperature cure. The latter structure has been found to exhibit excellent damping characteristics and high peel strength [35].

The toughness-morphology dependence, in terms of volume fraction, particle size distribution of the dispersed phase and the particle/matrix interface characteristics for two types of rubber-toughened √epoxies, i.e. CTBN and ATBN modified resins, has been investigated using several techniques by Kunz and co-workers [35]. The amount of rubber added to the bisphenol-A epoxy resin was varied in both cases between 5 and 15 parts by weight. It was found that ATBN rubbers produce a diffuse interface between the dispersed rubber phase and the epoxy matrix, in contrast to the sharp boundaries at the interface of CTBN particles. The difference in interface structure has been attributed to ATBN particles having highly irregular shapes compared to the nearly spherical CTBN particles. A few years later Yamanaka *et al.* [36] showed that the ATBN particles are somewhat interconnected owing to gelation of the matrix occurring before the spinodally decomposed rubbery phase fully develops into separate spherical particles. Bimodal particle size distributions, as well as a marked increase in the number of large particles (> 200 nm), were observed with both modifiers with increasing rubber content. Both rubber modifiers, unexpectedly from the difference in particle geometry, were found to have essentially identical toughness, which corresponded to greater than a five-fold increase over the pure epoxy. For both modifiers toughness seems not to increase with rubber content over the range 5–15 pph.

The use of amine-terminated rubber modifiers is attractive because of the high reactivity of the end groups toward the epoxide ring which will result in shorter gel times.

The influence of curing temperature on morphology and mechanical properties of blends obtained by adding different amounts of ATBN to a bisphenol-A type epoxy resin has been studied by Butta *et al.* [37] who found that the final morphology of the toughened systems is strongly dependent on cure temperature and rubber content. Curing at low temperature promoted the formation of optically clear materials, although DSC data and dynamic-mechanical tests have revealed the presence of a two phase structure, albeit highly interdiffused. The temperature at which clear materials were obtained was found to increase with increasing rubber content. Curing at high temperatures, on the other hand, gave rise to the formation of large spherical domains. With increasing ATBN content these domains became bigger and more closely packed, reaching phase inversion conditions above 20% rubber. The volume fraction of precipitated phase, determined on SEM micrographs, was found to be higher than the amount of added oligomer, which confirms the presence of epoxide chains in the displaced particles.

CURING MECHANISM OF CTBN MODIFIED EPOXY RESINS

A typical formulation of an epoxy resin toughened with CTBN is: 100 parts DGEBA epoxy resin, 10 parts CTBN oligomer, 5 parts piperidine catalyst/hardener.

Infrared (IR) studies have shown that the oligomeric dicarboxylic acid first forms a salt with the amine [38] which is responsible for phase separation leading to particle precipitation. The carboxylate salt, in fact, will subsequently react very rapidly with the epoxy groups of the resin. Since the latter is present in a large excess, reactions will take place also directly between the epoxy groups of the resin and the amine groups of the hardener, but at a much lower rate, thereby allowing the reaction products containing the carboxylic acid component to reach gelation conditions first and create the required fluctuations of concentration to induce phase separation by spinodal decomposition.

In addition to causing phase separation, the curing reactions lead to an increase in viscosity, and eventually to gelation of the entire resin mixture. The resulting reduction in molecular mobility lowers the rate of reactions. At 120°C, the epoxy resin–piperidine–CTBN system demixes during the first 60 min of the curing reaction, but shows no evidence of further phase separation thereafter. It therefore appears that phase separation is confined to the early stages of curing, and stops well before the matrix resin reaches the gel point.

Although the improvement in toughness of rubber-toughened DGEBA epoxies can be quite large, not all thermosets or not even all epoxy resins can be toughened by the above technique, as they may not be capable of adjusting the kinetics of the reactions to cause the precipitation of the toughening particles. Moreover, the improved toughness of epoxies (as mentioned earlier) arises mainly from shear deformation in the matrix, which is dependent on the cross-link density and intrinsic chemical structure [39].

It is important to note that often the precipitation of the toughening particles can be induced by pre-reacting the oligomer with an excess of epoxy resin prior to the addition of the hardener [24]. A selective catalyst, such as triphenyl phosphine, can be used in the first step to produce an A–B–A activated block copolymer of much higher molecular weight than the surrounding unreacted epoxy resin/hardener, which will give rise to a binodal type of phase separation with the formation of small particles that will grow in size until the process is arrested by the gelation of the surrounding matrix.

GLASSY POLYMERIC TOUGHENING AGENTS

Although CTBN and ATBN oligomers are very efficient for improving the fracture properties of epoxy resins without sacrificing excessively the modulus and strength, these two elastomeric modifiers have some drawbacks. The main deficiency of these oligomers is the high level of unsaturation in their structure, which provides sites for degradation reactions in oxidative and high temperature environments [40]. The presence of double bonds in the chains can cause oxidation reactions and/or further cross-linking with the loss of elastomeric properties and ductility of the precipitated particles.

Several attempts have been made over the last two decades to find alternative modifiers to CTBN and ATBN for the toughening of epoxy resins.

In order to avoid deterioration in the inherent stiffness and strength and a reduction in the T_g of the resin, some engineering thermoplastics, e.g. PES and PEI, have been used to produce systems consisting of rigid ductile particles dispersed in the epoxy matrix.

Polyethersulphone has a high glass transition temperature (*ca* 225°C), possesses an excellent chemical resistance and is stable at high temperatures. Because of the high molecular weight of these polymeric modifiers, the rate at which they can be dissolved in an epoxy resin is rather low for an industrial process. Hence they have to be added from a solution and the solvent has to be evaporated prior to the addition of the hardener.

Raghava [41] has blended a low molecular weight polyethersulphone (PES) containing hydroxyl end groups with a tetrafunctional epoxy resin, expecting the reactive end groups of PES to participate in the chemical reactions during curing of the epoxy resin and to achieve in this way a high level of interfacial adhesion. The increase in toughness that has been achieved with these epoxy-polyethersulphone systems, however, was only marginal.

Bucknall and Partridge [42, 43] have confirmed the results reported by Raghava and have also found only a small increase in fracture toughness for mixtures of PES with tetrafunctional and trifunctional epoxy resins, separately cured with diaminodiphenylsulphone (DDS) and dicyandiamide (DICY). They also reported that the PES-toughened tetrafunctional epoxy resin cured with both type of hardeners did not show phase separation, whereas phase separation was observed in the case of a trifunctional resin.

Diamont and Moulton [44] have also investigated the toughening of a tetrafunctional epoxy resin using various ductile thermoplastic polymers possessing a high glass transition temperature. They observed that a mixture of epoxy resin and PES did not possess a two-phase structure and that the fracture toughness of the modified system was not markedly different from the values measured for unmodified epoxy.

The miscibility of a polyethersulphone and a tetrafunctional epoxy, cured with an aromatic anhydride, was examined in further studies by Raghava [45] using scanning electron microscopy and dynamic mechanical spectroscopy. This author has also considered the influence of the morphology of the epoxy/PES blend on fracture toughness and toughening mechanism. The modified system exhibited a two-phase bimodal particle distribution morphology even though the dynamic mechanical spectroscopy analysis showed only one α relaxations peak due to the close proximity of the T_g values of the two components. As in previous studies, the same author found a lack of enhancement in low temperature fracture toughness values for PES modified epoxy resin. This was again attributed to the very high cross-link density of the cured tetrafunctional epoxy and to the possibility that the inclusion of low concentrations of PES is not sufficient to produce formation of shear bands. The Young's modulus of the modified system was found to be slightly lower than the values for the neat epoxy resin, possibly due to a reduction in cross-linking density as a result of the dilution effect of the uncross-linked PES chains.

Hedrick *et al.* [46] used phenolic hydroxyl and aromatic amine end functionalities in poly(arylene ether sulphone) oligomers to chemically modify the network of a difunctional DEGBA resin. The oligomers reacted with a large molar excess of epoxy resin and then cured into cross-linked networks with a stoichiometric quantity of 4,4′-diaminodiphenylsulphone (DDS). The aryl ether sulphone was found to be molecularly miscible with the epoxy precursor over the entire range of compositions and molecular weights investigated, developing a two phase structure during curing, in which polysulphone formed discrete particles evenly dispersed in the epoxy matrix. Despite the existence of a two-phase structure, the cross-linked systems were nearly transparent, due to a similarity in refractive index of the two components. The fracture toughness of these resins was improved significantly with a minimal deterioration in the flexural modulus. The authors attributed this result to the presence of strongly adhering polysulphone particles in the epoxy matrix, which deformed plastically during fracture and induced shear yielding in the epoxy matrix. Similar improvements have been reported more recently by Yoon and co-workers [47] using aminophenyl terminated polyethersulphone in a difunctional bisphenol-A epoxy resin. The latter studies have provided the evidence for the hypothesis relating the brittleness of trifunctional and tetrafunctional epoxy resins to their higher cross-linking density which prevents the occurrence of yielding deformations in the matrix.

Martuscelli and co-workers [48] have used a bisphenol-A based polycarbonate (PC) as the glassy thermoplastic polymer modifier. The PC was dissolved directly in the uncured epoxy resin at high temperatures (220°C). After the addition of the curing agent and the accelerator at lower temperatures (80°C), the temperature was increased again for curing and subsequently for post-curing. FTIR analysis on the uncured epoxy/PC mixtures revealed the occurrence of chemical interactions between the two components producing PC chains with epoxide end groups. These functional groups take part in the subsequent cross-linking reactions, resulting in the incorporation of PC segments within the epoxy network. Dynamic mechanical measurements and scanning electron microscopy (SEM) analysis of the epoxy/PC blends did not show any evidence of phase separation of the minor component during the curing process. Tests at both low and high strain rate showed a marked increase in toughness with increasing amount of PC in the blend. In particular, for low speed tests the addition of 20 wt% of PC increases the toughness of the epoxy matrix by a factor of about seven, while for the high speed tests the increase is about five-fold. Moreover, this toughening effect with the use of PC was achieved without significantly reducing other desirable properties of the matrix such as the elastic modulus. From SEM analysis it was found that localized yielding occurs at the crack-tip and that the mechanism is probably similar to what is normally observed with interpenetrating network modifications.

TOUGHENING AGENTS BASED ON RIGID CRYSTALLINE POLYMERS

In the previous section it was pointed out that the addition of glassy rigid polymers to epoxy resins has been found to be successful only in a limited number of cases. A relatively high fracture toughness was obtained, in fact, only when the morphology became a two-phase co-continuous microstructure or when the thermoplastic component became the continuous phase with dispersed epoxy domains. This type of distribution of the glassy polymer rich phase can lead to poor high temperature creep resistance and/or reduced solvent resistance. On the other hand, if a rigid crystalline phase forms a co-continuous dispersed phase in the epoxy network these deficiencies could be eliminated, but it is difficult to visualise how such rigid crystalline domains can provide an efficient toughening mechanism.

One possible toughening mechanism in such systems could operate by phase transformation, which is well known for ceramic materials [49]. An example is represented by zirconia-containing ceramics [50–55]. The metastable tetragonal phase of zirconia is incorporated into the ceramic, and under the influence of the stress field ahead of a crack tip, this phase transforms to the stable monoclinic phase. Because the monoclinic phase is less dense than the tetragonal phase, compressive stresses are set up on to one of the phases, which superposes on the tensile stress field ahead of the crack tip producing shear deformations, which have the effect of increasing the critical fracture energy.

Such a toughening mechanism might be applicable to brittle polymers if a stress-transformable crystalline polymer were used as the rigid second phase and might well provide an effective solution to the toughening of highly cross-linked thermosets. However, only a few studies have been carried out to verify this hypothesis for polymeric materials [56]. For dispersed crystalline polymers to be effective for toughening by phase transformation, several properties similar to those of the metastable tetragonal phase of zirconia are required. First, the polymers should be able to exist in a variety of crystalline states and transformations from one state to another should take place under the influence of an applied stress. The desired phase transformation is one in which volume dilation and distortion both occur in response to the stress field ahead of a crack tip. Second, the desired stress-free crystalline phases should be stable in the temperature ranges under which the brittle matrix resins are processed. Third, these polymers should form strong interfacial bonds with the matrix.

Kim and Robertson [2] studied the toughening of an aromatic amine-cured diglycidyl ether of bisphenol A epoxy with particles of crystalline polymers. The crystalline polymers chosen were poly(butylene terephthalate) (PBT), nylon 6 and poly(vinylidene fluoride) (PVDF). Each of these was found to be capable of undergoing phase transformation as the result of the application of a stress field, and each of these polymers could be bonded to epoxies. For the case of PVDF, however, an amine curing agent is necessary to achieve a good bond with the epoxy resin. The authors reported that nylon 6 and PVDF were found to toughen epoxy resins to an extent similar to what is achievable with an equivalent amount of CTBN rubber. Fracture toughness, on the other hand, was increased two-fold by the inclusion of PBT over that achieved with nylon 6 and PVDF. From microscopy studies the above authors found that the toughness of PBT-epoxy systems was independent of particle size, for particles in the range of 10s of micrometres, while the toughness of nylon 6-epoxy systems decreased with increasing particle size, for particles smaller than about 40 μm. There was no reduction in either modulus or yield strength of the epoxy resin with the inclusion of either nylon 6 or PBT and a lower reduction of such properties was observed with the inclusion of PVDF than with the inclusion of rubber.

In a recent work, Kubotera and Yee [57] investigated the possibility of using a crystalline block copolymer, containing amorphous end chains, as a modifier to improve the fracture toughness of high cross-linked epoxy resins. They reported that both polyetheretherketone (PEEK) and PBT units can form crystals in the form of triblock copolymers with amorphous PES. The DSC curves and the micrographs showed that even a short chain length of PBT and PEEK units, having only three and four repeating units, can form a crystalline phase. The main reason for using copolymers rather than crystalline homopolymers was that the copolymer particles were expected to exhibit better interfacial adhesion, owing to the solubility of the amorphous blocks. All copolymers, in fact, gave homogeneous resin mixtures with loadings up to 15–20 wt%, resulting in multiphase structures after curing. The SEM micrographs revealed the presence of a second phase dispersed in the epoxy matrix, which did not result from spontaneous liquid–liquid phase separation, but from crystallization growth. The results showed, however, that the overall behaviour was not very different from that of the unmodified systems. The most effective modifier, in terms of toughness, appeared to be the triblock PEEK–PES–PEEK system, which gave almost a single phase structure from optical microscope observations.

ACRYLIC ELASTOMERIC OLIGOMERS

Banthia *et al.* [58] have used various carboxyl terminated elastomeric acrylate oligomers to toughen a DGEBA resin. They have found that acrylate oligomers exhibit extremely good miscibility with conventional epoxy resins, and will precipitate as a distinct dispersed phase during curing. With the addition of 4–10 wt% of ethylhexyl acrylate oligomers, the cured castings were found to exhibit enhancements in impact strength comparable to traditional toughened epoxy systems. In essence the above authors have found that carboxyl-terminated telechelic ethylhexyl acrylate oligomers are effective elastomeric toughening agents, exhibiting better oxidative and thermal stability with respect to CTBN toughening systems.

Wang *et al.* [13] used as modifiers novel polyfunctional acrylate elastomers with medium molecular weight to toughen epoxy resins. The polyfunctional poly(n-butylacrylates) reported in their study were epoxy functionalised poly(n-butylacrylate) (ETPnBA) and carboxyl functionalised poly(n-butylacrylate) (CTPnBA), both obtained by photopolymerization. The effect of the level of functionality and type of functional group in the elastomers used as toughening agents was investigated by means of tensile and impact tests and electron microscopy. It was found that there is an optimum functionality of elastomers for maximum impact resistance in epoxidised (ETPnBA) and carboxylated (CTPnBA) copolymer-modified systems. Studies on morphology of the modified epoxy resin system indicated that the better toughening effects of the epoxy functionalised modifier ETPnBA was due to the presence of a multiple distribution of particles sizes. The aggregation of rubber particles occurring with the use of carboxyl functionalised CTPnBa in the epoxy resin, on the other hand, was believed to be the cause of the observed reduction in toughness.

Lee and co-workers [59] obtained similar results by using a family of n-butyl-acrylate/acrylic acid (nBA/AA) copolymers with a broad functionality range (1.62–9.93). They reported, in fact, that improvements of adhesion strength could be achieved by incorporating the nBA/AA copolymer in a DGEBA epoxy matrix and that an optimum functionality existed to achieve the highest interfacial adhesion.

A different approach was taken by Touhsaent *et al.* [60]. These workers have synthesised two polymers, one of which formed a network, by simultaneous independent reactions in the same container. They have indicated that inter-cross-linking reactions are eliminated by combining free radical (acrylate) and condensation (epoxy) polymerisation. By this method they modified an epoxy resin with poly(n-butyl acrylate) polymer. They have found that a two-phase morphology developed, consisting of co-continuous rubber domains (about 0.1–0.5 μm), within the epoxy resin. The dimensions of the dispersed rubber phase domains and the extent of molecular mixing between the two components were found to depend on the relative reaction rates (or gel times) in relation to the rate of phase separation. Better mechanical properties resulted when the extent of molecular mixing was minimised and heterophase semi-IPNs were produced.

Similar observations were reported by Sperling *et al.* [61] in their work concerning the production of heterogeneous IPNs of polymethylmethacrylate (PMMA) within a polydimethyl siloxane elastomer (PDMS). When polymerisation of the network forming methacrylate monomer and cross-linking of the PDMS elastomer were carried out simultaneously, the resulting product was found to contain dispersed PMMA particles within the PDMS matrix giving rise to a strain-hardening elastomeric behaviour.

When the methacrylate monomer was polymerised within an already cross-linked PDMS phase, the resulting product displayed a co-continuous two-phase morphology and exhibited a leathery type behaviour.

HYGROTHERMAL TOUGHENING AGENTS

The search of functionalised oligomers for the production of toughened epoxy resins exhibiting low water absorption characteristics and that are suitable for high temperature applications has been the focus of attention of several research workers.

For example Takahashi *et al.* [62] have examined several amine terminated silicone oligomers as toughening agents for epoxidised novolac resins for use as encapsulants for semiconductor integrated circuit devices, i.e. low electrical stress application. In such cases siloxane oligomers offer the following advantages: (a) lower T_g values for the dispersed rubbery particles than conventional elastomers; and (b) very good thermal stability. The miscibility of the silicone oligomers with epoxy resin was found to increase with increasing ratio of phenyl methyl siloxane units relative to dimethyl siloxane units in statistical copolymers. Total solubility in the epoxy resin was achieved, however, only in the case of phenyl methyl siloxane homopolymers which produced transparent (monophase) cured products. For other siloxane oligomers a two-phase morphology was observed in every case, but the dispersed particles became extremely small (i.e. about 0.01 μm) when the silicone oligomers were added to the resin as solutions in toluene.

It is interesting to note that lower thermal expansion coefficients were observed for these systems in compositions containing 70% fused silica filler. This has been attributed, however, to improved interfacial adhesion resulting from reactions between the siloxane component and the silica particles, thereby improving the transfer efficiency of the thermal stresses.

Siloxane elastomers have been chosen also by other workers as an attractive alternative to traditional toughening systems, although some of these oligomers are quite expensive. Besides the advantages already mentioned, they exhibit good weatherability, oxidative stability, high flexibility and moisture resistance [63]. Moreover, the non-polar nature and low surface energy of siloxanes constitute a thermodynamic driving force for them to migrate to the air–polymer interface. This migration can occur with simple physical blends as well as with systems containing chemically linked microphase-separated segments. During the early stages of curing of a siloxane-modified epoxy, i.e. before extensive cross-linking begins to impair the diffusion characteristics, such migration is considered possible and is believed to lead to the formation of a very hydrophobic and chemically bound surface coating [64]. There is evidence to suggest that such a surface layer reduces friction and improves the wear properties [65].

Yorkgitis and co-workers [66] have chemically modified epoxy resins with functionally terminated poly(dimethylsiloxane), poly(dimethyl-co-methyltrifluoropropyl siloxane) and poly(dimethyl-co-diphenyl siloxane) oligomers and have analysed the morphology, solid-state properties and friction and wear properties of the systems. They have found that the miscibility of siloxane modifiers in epoxy resins can be enhanced by increasing the percentage of methyltrifluoropropyl (TFP) siloxane or diphenyl (DP) siloxane relative to dimethyl siloxane.

It is known that the solubility parameter is a good indicator of the miscibility of one substance with another and, together with considerations on molecular weight and temperature, can be used to predict the possible occurrence of phase separation of the elastomer from the resin during cure. Through copolymerization of dimethyl siloxane with partially aromatic diphenyl siloxane or polar methyltrifluoropropyl siloxane, it is possible to raise the solubility parameter of the siloxane elastomer from $3.7 \cdot 10^{-3}$ $(J/m^3)^{1/2}$ close to that of the epoxy resin, approx. $4.5 \cdot 10^{-3}$ $(J/m^3)^{1/2}$ [1]. This is analogous to the manner in which the solubility parameter of ATBN and CTBN elastomers are controlled by adjusting the acrylonitrile content. In this way the level of miscibility of the siloxane modifier in the epoxy resin controls the size and make-up of the phase-separated elastomeric domains, i.e. the morphology and the resulting modulus and fracture toughness of the modified resin. The authors have reported that, while unmodified polydimethylsiloxane, due to the large difference in solubility parameter, phase separates from the epoxy resin into large domains which do not increase the fracture strength, the fracture toughness of the epoxy resin can be improved by modification with siloxanes containing 40% or higher methyltrifluoropropyl content, or 20 and 40% diphenyl content.

Cecere *et al.* [67] have focused their work on the optimisation of both molecular weight and diphenyl contents of the poly(diphenyl-dimethyl) siloxane oligomers in order to obtain the maximum impact strength in the modified epoxy networks without sacrificing the flexural modulus. They have found that siloxane copolymers when used as impact modifiers are not very effective in increasing fracture toughness over that of an unmodified system. It appears that a system incorporating 15 wt% of a 40% diphenyl/60% dimethyl-copolymer with a molecular weight of approx. 5000 g/mol yields the highest impact strength with a small decrease in flexural modulus. This system phase-separates into evenly dispersed particles with an average diameter of *ca* 1 μm.

As epoxy and silicone rubber are completely immiscible, the addition of a compatibiliser is necessary to obtain a satisfactory dispersion of the rubber in the resin.

The main objective of Kasemura and co-workers [68] was to find an appropriate surface active agent to reduce the interfacial tension between the resin and the rubber, in order to compatibilise the two components. These authors achieved adequate compatibility in the epoxy resin with the use of a polyether modified silicone oil (EtMPS) to disperse an RTV (room temperature vulcanising) silicone rubber or silicone diamine. The results showed that the impact fracture energy of the resin was increased by the addition of the RTV silicone rubber up to two times that of the unmodified resin, while the addition of silicone diamine had almost no effect, possibly because the molecular weight was too low. Moreover, T-peel strengths of aluminium plates bonded by epoxy resin filled with RTV silicone rubber and with silicone diamine effectively increased with the silicone content, showing a maximum at 10–20 pph. By a scanning electron microscope, many particles of silicone rubber, 1–20 μm, were observed across the whole of the fracture surface.

More recently other workers [69] have studied the rubber-modification of bifunctional and tetrafunctional epoxy matrices by means of a block copolymer of polydimethylsiloxane and polyoxyethylene (PDMSO-co-PEO) elastomer or an anhydride-grafted polybutene (PB-g-SA). The choice of these types of liquid reactive elastomers was determined by their higher thermal and photo-oxidative resistance compared with classical unsaturated elastomers. The results showed that the mechanism of fracture of bifunctional resins can be positively influenced by the addition of the above mentioned rubbery systems, while for a tetrafunctional epoxy resin, like TGDDM, the same elastomers do not produce any improvement in impact properties. The above authors have attempted to give an explanation on the basis of the different networks obtained in the two matrix systems. In accordance with previous findings and interpretations the authors concurred that in the case of TGDDM the resin has a very high cross-link density and, therefore, its capacity to deform by shear yielding is highly reduced, hence the contribution of the rubbery particles to enhance fracture toughness by promoting localized shear yielding in the matrix is rather small.

The constant search for new elastomeric systems with specific properties to use as toughening agents for epoxy resin, has induced some researchers to investigate the possible use of fluoro elastomers.

Attempts to introduce fluorine atoms into the network of cross-linked epoxy formulations have been made through the addition of specially functionalised fluoroelastomers with the aim of enhancing simultaneously the toughness and thermal stability characteristics [70]. The elastomer and the resin/hardener components were mixed from solutions to obtain an initially monophase system which would subsequently allow the precipitation of the elastomer into fine particles through post-curing heat treatments. Mijovic *et al.* [71] have grafted functional groups onto a fluorocarbon elastomer to enhance their miscibility and reactivity with epoxy resins. A large increase in fracture energy was observed with the addition of 15% elastomer to the resin, though this was accompanied by a decrease in T_g, due to the solubilisation of some of the elastomer within the epoxy network.

By reacting in solution an acid fluoride functionalised perfluoroligomer with a diglycidyl ether of bisphenol A, Rosser *et al.* [22] have produced a prepolymer which was subsequently used to modify an epoxy/diaminodiphenylsulphone resin matrix for a glass cloth composite. They have demonstrated that this immiscible elastomeric prepolymer exhibits sufficient chemical reactivity with the epoxy resin to give rise to improvements in flexural ductility and impact resistance, without loss of strength and modulus or lowering the glass transition temperature. The results suggest that a simultaneous interpenetrating polymer network (SIN) was formed which gave rise to improvements in the mechanical properties of the composite.

The use of modified perfluoropolyether oligomers in an epoxy resin was found by Mascia *et al.* [24] to produce both co-continuous and particulate two phase systems, the morphology depending on procedure details. Hydroxyterminated fluoroalkene oxide oligomers were reacted with chlorendic anhydride and subsequently with ε-caprolactone to produce carboxyl-terminated perfluorether prepolymers that were totally miscible with diglycidylether of bisphenol A. Curing the epoxy resin mixtures with hexahydrophthalic anhydride hardener and benzyl dimethylamine catalyst produced transparent products exhibiting a co-continuous two-phase (heterogeneous IPN) morphology. Pre-reacting the fluoroalkenoxide prepolymers with an excess of epoxy resin, prior to the addition of hardener and catalyst, resulted in opaque products displaying a two-phase dispersed particle morphology. Optical microscopy experiments on the resin mixture up to the gelation point have clearly revealed that particles form and grow only if "nuclei" are originally present. The nuclei can be considered of consisting of small swollen "gels" which grow into particles as a result of the inner diffusion of the hardener. Mechanical property measurements revealed for both systems remarkable improvements in fracture energy (450–600%), flexural strength (24–75%) and strain at break (300–500%), even with the use of only small amounts of perfluoropolyethers, i.e. 3.5–5.0%. However, these were achieved at the expense of a small decrease in modulus (20–30%) and T_g (10–25°C). It must be noted that these effects were much more pronounced for products exhibiting a two-phase, dispersed particle morphology, than for co-continuous phase (IPN) systems. The above authors [25] also found that both IPN and particulate two-phase formulations showed a reduction in flexural strength after 21 days ageing at 200°C, but the measured values were always much greater then for the non-aged control samples. The strain at break for IPN systems, however, increased considerably with ageing in proportion to the concentration of prepolymer used.

CONCLUDING REMARKS

From an analysis of the literature on modifiers for epoxy resins and from a consideration of the more general interpretation of the mechanisms for energy absorption in polymer blends, it is possible to arrive at the following conclusions for toughening of epoxy resins.

(a) An efficient toughening mechanism can be set up only if the cross-linking density is sufficiently low to enable the resin to undergo localised plastic deformations under a shear dominated stress field.

Soft or rubbery inclusions, whose surface-to-surface distance is below a critical value, are propensive to inducing shear deformations in the matrix and will, therefore, provide the required conditions for toughness enhancement.

Such conditions are more likely to be fulfilled with a multimodal particle size distribution.

(b) When the cross-linking density is high, as in the case of tetrafunctional resins, toughness can be increased with the use of ductile glassy polymers capable of reacting with the epoxy resin in order to produce a strong interfacial adhesion between the two phases.

The similar modulus of the two phases creates a uniform stress distribution across the boundaries.

As a result fracture is not likely to initiate near the boundaries, but within the matrix. The propagation of cracks will be hampered by plastic deformations or microcavitations in the dispersed ductile particles.

Obviously such a mechanism will operate more effectively if the two phases are co-continuous and/or the interfacial adhesion is sufficiently high to prevent fracture from propagating at the interphase boundaries.

A cautionary remark is necessary, however, in relation to the ability of the glassy thermoplastic phase to undergo plastic deformations. It has to be borne in mind, in fact, that when the glassy polymer precipitates out it will contain a certain amount of dissolved resin and hardener which are likely to give rise to plasticisation and antiplasticisation. The latter results in a depression of β-relaxation and severe embrittlement will take place as a result of the reduction in critical crazing strain [72, 73], thereby impairing their energy absorption characteristics through plastic deformations.

(c) The miscibilisation of oligomers through telechelic end-of-chain extensions is likely to constitute the most efficient mechanism for the nucleation of particle precipitation during curing of the resin. These are also likely to minimise reductions of the T_g of the matrix by residual (non-precipitated) oligomeric species owing to their inability to form true solutions in the resins but only highly swollen molecular aggregates. Consequently phase separation by nucleation and growth during curing is likely to occur very readily and completely.

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