

Rubber Toughened Epoxy

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Abstract: Toughening of epoxy resins for improvement of crack resistance has been the subject of intense research interest during the last two decades. Epoxy resins are successfully toughened by blending with a suitable liquid rubber, which initially remains miscible with epoxy and undergoes a phase separation in the course of curing that leads to the formation of a two-phase microstructure, or by directly blending preformed rubbery particle. Unlike the situation for thermoplastics, physical blending is not successful for toughening epoxy resins. Recent advances in the development of various functionalized liquid rubber-based toughening agents and core-shell particles are discussed critically in this review.

Keywords: epoxy, toughening, liquid rubber, blending, phase separation.

Introduction

Epoxy resins are unique among all the thermosetting resins due to several factors^{1,2} viz. minimum pressure is needed for fabrication of products normally used for thermosetting resins, shrinkage is much lower and hence lower residual stress in the cured product than that encountered in the vinyl polymerization used to cure unsaturated polyester resins, use of a wide range of temperature by judicious selection of curing agent with good control over the degree of crosslinking, availability of the resin ranging from low viscous liquid to tack free solid etc. Because of these unique characteristics and useful properties of network polymer like high strength, very low creep, excellent corrosion and weather resistance, elevated temperature service capability and adequate electrical properties, epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates etc.¹⁻⁴

The major drawback of epoxy resins is that in the cured state they are brittle materials having fracture energies some two orders of magnitude lower than engineering thermoplastics and three orders lower than metal.⁵ This inherent brittleness causes the poor damage tolerance to impact of the composites made from epoxy resin and poor peeling and shear strength of epoxy based adhesive. Hence toughening of

epoxy resins has been the subject of intense investigations throughout the world. The epoxy resins are most successfully toughened by incorporating a rubbery filler as a distinct phase of microscopic particles. This can be achieved in two ways : 1) blending with functionalized liquid rubber having restricted solubility which is miscible initially, with the epoxy hardener mixture and undergo phase separation at a certain stage of the curing reaction leading to two phase microstructure 2) by dispersing preformed rubbery particles directly in the epoxy matrix without undergoing phase separation.

Toughening by Liquid Rubber

Though patented earlier, rubber toughened epoxy is first reported in the scientific literature by McGarry and Willner⁶ in 1968, using low molecular weight carboxyl terminated copolymer of butadiene and acrylonitrile (CTBN, Goodrich) as a liquid rubber. They used CTBN and various diglycidyl ether of bisphenol A (DGEBA) epoxies cured with piperidine (PIP) to get a network having two-phase microstructure and reported a ten-fold increase in fracture toughness. Following this pivotal work, extensive work has been done in the last two and half decades to understand the principle of morphology development, morphology and fracture property relationship and the mechanism of toughening etc. Various new types of toughening agents have also been investigated as a replacement for CTBN.

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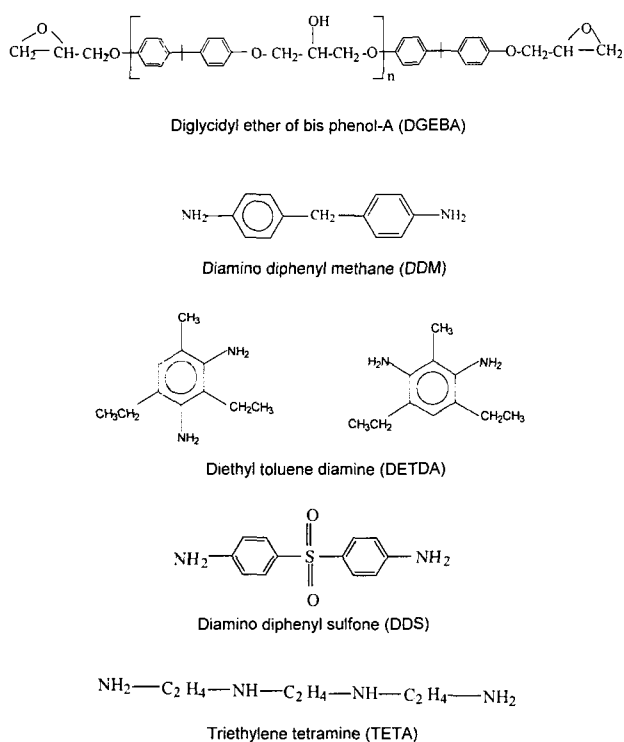


Figure 1. Chemical structures of epoxy and amine curing agents.

The modified epoxy resins have been characterized with respect to their fracture behavior in bulk and adhesive bonds and the results have been reported in the literature as peel strength, resistance to peel force, impact strength, resistance to crack propagation, fracture toughness, critical strain energy rate. These terms may refer to different type of experiments; all related to the same materials property i.e. the resistance to mechanical and thermal shock. The review of rubber toughened epoxy is somewhat complicated by several factors. The amount of literature on this two-phase system has increased in number and scope. For example, the work includes different types of curing agents (amines, anhydrides) as well as a variety within each type. The chemical structures of difunctional epoxy resin and some important amine curing agents are shown in Figure 1.

Chemistry

For effective toughening, the liquid rubber is required to be chemically bonded to the epoxy matrix.^{7,8} Because weak bonding between the matrix and the rubber particles may cause debonding of the particle leading to the failure of the toughened system. Moreover, collection of free liquid rubber molecules at the metal interface can acts as a weak boundary layer in the adhesive joints leading to substantial decrease in adhesive joint strength.^{9,10} Siebert and Riew¹¹ first described the chemistry of rubber particle formation in an admixed model involving CTBN, a DGEBA liquid epoxy resin and a

piperidine (PIP) catalyst. They proposed that the composition of rubber particles in the dispersed phase critically depended upon the in situ formation of the epoxy-CTBN-epoxy adduct which is then further chain extended and crosslinked with additional epoxy resin. The progression provides a chemical bond between the dispersed rubber phase and the matrix resin. This occurs with a curing agent like PIP which catalyses the carboxyl-epoxy reaction i.e. a selective catalyst.

However, most of the curing agents favor epoxy-amine reaction and the carboxyl-epoxy reaction is suppressed. This problem has been resolved^{12,13} by prereacting the liquid rubber and the epoxy resin in an alkyl hydroxyl esterification reaction in presence of a catalyst like tri-phenyl phosphene. These acid adducts can now be cured with any curing agent because they only contain epoxy groups and capable of reacting in the similar way as epoxy resin. The reaction is illustrated in Figure 2. N. C. Paul *et al.*,¹⁴ in their study with ambient temperature cured adhesive, found that prereaction of CTBN and epoxy is essential for toughening as at ambient temperature carboxyl-epoxy reaction does not take place.

Compatibility and Morphology

The liquid rubber is compatible with epoxy resin before curing at the curing temperature.¹⁵ The thermodynamic condition for compatibility is that free energy change of mixing

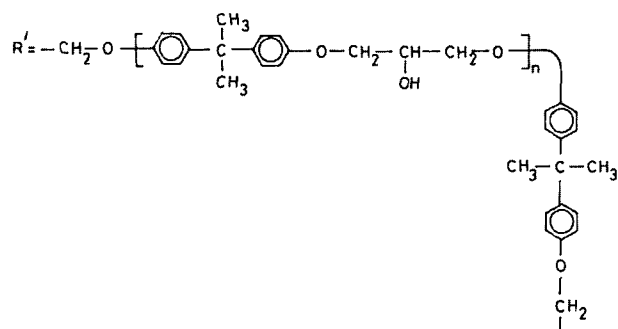
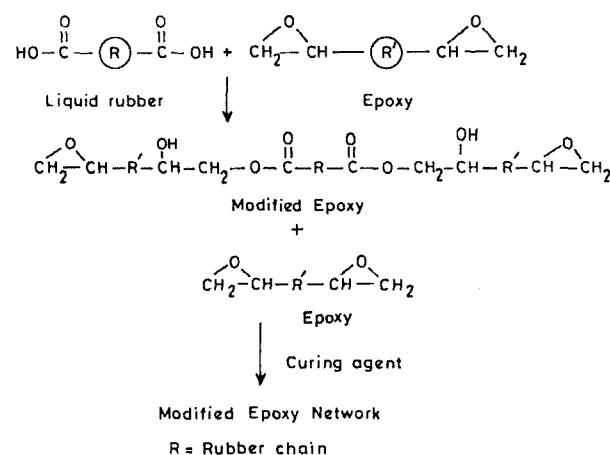


Figure 2. Prereaction of liquid rubber with epoxy and curing.

should be negative^{15,16} :

$$(\Delta G_m)_{P,T} < 0 \quad (1)$$

Combining the Flory- Huggins equation and the Hildebrand equation,¹⁷ the free energy of mixing can be expressed as :

$$(\Delta G_m)/V = \phi_e \phi_r (\delta_e - \delta_r)^2 + RT(\phi_e/V_e \cdot \ln \phi_e + \phi_r/V_r \cdot \ln \phi_r) \quad (2)$$

where ϕ_e , ϕ_r are the volume fractions and δ_e , δ_r are the solubility parameters and V_e and V_r are the molar volume of epoxy and rubber respectively.

Since both ϕ_e , ϕ_r are fractions the second term is always negative. For a fixed epoxy /rubber composition, ΔG_m at constant temperature depends on δ , i.e. the chemical nature of rubber and V_r , which is dependent on molecular weight of the rubber. Proximity of δ_e and δ_r and low molecular weight favors the mixing process. If these two parameters are controlled in such a way that ΔG_m is marginally negative then the rubber will be compatible with epoxy before the curing but with the advancement of curing reaction, V_e & V_r will increase due to increase in molecular weight of rubber and epoxy and at a certain stage ΔG_m will become positive. At that point rubber starts undergoing phase separation called cloud point.

Hence phase separation process can be described¹⁸⁻²⁰ as shown in Figure 3. Initially ($p = 0$) the system is homogeneous, phase separation starts at the cloud point conversion p_{cp} and final morphology is arrested at gelation (p_{gel})^{21,22} (in fact well before gelation) due to tremendous increase in viscosity, though some changes in phase composition after gelation is also reported.^{18,23} For complete phase separation the phase separation time (t_{ps}) has to be higher than the time required for diffusion of rubber from epoxy medium (t_{diff}). The diffusivity is the controlling factor of phase separation

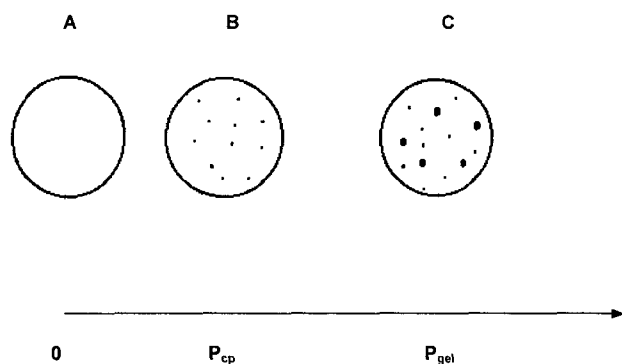


Figure 3. Stages during the phase separation process: (A) Homogeneous solution for the unreacted system, (B) Beginning of phase separation at cloud point conversion (P_{cp}), (C) Final morphology at P_{gel} .

if t_{diff} is greater than t_{ps} . The diffusivity of rubber in epoxy medium is considered to be proportional to the temperature viscosity ratio through Stokes-Einstein equation²⁴:

$$D_{er} = kT/6\pi R_r \eta_e \quad (3)$$

where k is the Boltzman constant, R_r is the radius of rubber adducts, η_e is the viscosity of the medium and T is absolute temperature. The characteristics time scale for diffusion in two dimensions is

$$t_{diff} = L^2 / 2 D_{er} . \quad (4)$$

a length scale (L) can be assigned from the average two-dimensional distance between domain centers obtained from micrographs of the cured specimen.

Manziona *et al.*^{25,26} calculated the t_{ps} and t_{diff} for epoxy/CTBN system using different initial cure temperature. They found that the initial cure temperature greatly affects the resulting morphology as it controls the diffusion of the rubber and gelation. The post curing temperature has no role on the resulting morphology, as phase separation is arrested at gelation. The effect of acrylonitrile content is also demonstrated.^{26,27} Generally, CTBN having higher acrylonitrile content has higher miscibility with the epoxy resin in terms of solubility parameter and undergoes phase separation at a later stage of curing and gives lower amount of phase separated rubber. CTBN with acrylonitrile content more than 30% results single-phase morphology.

Most of the author reported the discrete morphology for rubber modified epoxy system, which consists of spherical particle dispersed in the epoxy matrix.²⁵⁻²⁸ They have used a nucleation and growth mechanism to describe this morphology. William *et al.*^{29,30} developed a model to predict the fraction, composition and average radius of the dispersed phase segregated during the thermoset polymerization, based on the thermodynamic consideration as discussed above and the constitutive equation of the rate of nucleation, coalescence and growth. The variation in morphology with cure temperature as experimentally observed presumably results from the effect of temperature on the rate of nucleation and growth of the dispersed phase.²⁹⁻³³

Analysis of the experimental results on the effect of initial cure temperature and volume fraction of the rubber on the resulting morphology shows that the concentration of the dispersed phase particles decreases^{25,26,33} as the temperature increases; the volume fraction of the dispersed phase remains practically constant,^{23,32} decreases^{25,26} as temperature increases and the average particle diameter (\bar{D}) of the dispersed phase goes through a maximum^{25,33} or increases³⁴ as the temperature increases. The results were summarized in Table I.

These experimental results can easily be explained by the binodal phase separation model. The increase in \bar{D} with T_{cure} can be explained by considering the two factors : i) the

Table I. Effect of Increase in Cure Temperature (T_{cure}) on Particle Size of Toughened DGEBA Epoxy

Curing Agent	Modifier	Effect on Particle Size	Reference
DDM	CTBN	Increase	23
DDS	CTBN	Increase	36
DDS	CTBN	Increase	25, 34
DDM	CTBN	neutral	38
DETDA	HBP	decrease	78c, 78d
DETDA	CTPEHA	decrease	73c
TETA	ATBN	decrease	40b
DDM	Polyether sulfone	increase	40a

increase in thermodynamic driving force which depends on rate of epoxy reaction ii) diffusion rate of rubber particle from epoxy solvent which depends on the prepolymer viscosity. As the cure temperature increases the epoxy reaction rate increases and the viscosity decreases. Since the activation energy of curing reaction is higher than the same for prepolymer viscosity, the reaction rate increases more compared to the rate of diffusion. Hence the growth of rubber particles is favored. It is important to realize however, that for a large increase in temperature the situation may be different.^{36,37} For example, ΔG_m may be so high that the system remains completely miscible (no phase separation at all), or demixed particles do not attain large sizes due to the high system viscosity (arising from the high conversion levels). Therefore, \bar{D} vs. T_{cure} must show a maximum as has been experimentally observed.^{25,33,34} The variation of the dispersed volume phase with cure temperature can also be explained in the same way. The insignificant variation is due to the fact that the increase in both the diffusion coefficient and miscibility are somewhat counterbalanced.

On the other hand condition at which spinodal decomposition may be the origin of phase separation process have been discussed.³⁸⁻⁴⁰ This kind of phase separation is usually assigned to textures displaying some degree of connectivity, known as cocontinuous structure. Hsieh and Yamanaka *et al.*^{39,40} gave experimental evidence of the presence of spinodal decomposition in fast reacting systems with composition located close to the critical point (high rubber concentrations). Moreover Yamanaka *et al.*⁴⁰ stated that the nucleation-growth mechanism is not expected to take place in any case mainly because of the fact that nucleation is recognized to be very slow process. The spherical domain structure arises from evolution of an initial cocontinuous structure although no direct evidence of this model could be obtained.

Liquid Rubbers Other than CTBN

From the above discussion, it is apparent that it is the

presence of rubbery particles that toughens the epoxy matrix and it is not necessary that particles be made up of CTBN. Nitrile rubbers having other end groups like amine, mercaptan, hydroxyl etc. have also been examined.⁴¹ But among the reactive ended NBR rubbers, the CTBN gives the best performance.⁴² The better adhesive strength of the CTBN modified epoxy in comparison to other reactive group ended NBR modified epoxy can be attributed to the better adhesion with the substrate due to the presence of carboxyl group.

Rezaiford *et al.*⁴³ reported that significant toughness enhancement could be achieved by using poly(methyl methacrylate) (PMMA) grafted natural rubber instead of CTBN. Carboxyl terminated polyisobutylene⁴⁴ and polysulfide⁴⁵ rubbers are also reported as effective toughening agent for DGEBA resin using different types of amine hardener. Mizutani⁴⁶ has reported an anhydride cured transparent toughened epoxy network using hydroxyl terminated liquid polychloroprene rubber as toughening agent. The modified network containing 0-10 vol% of liquid rubber complete phase separated microstructure. However, the modified networks are transparent, because refractive index of rubber is comparable with that of epoxy.

Epoxy group containing triglyceride oils viz. Vernoria oil, epoxidized soybean oil and castor oil have been used as modifier for epoxy resin.^{47,48} Direct mixing of epoxidized oil and epoxy resin followed by curing of the mixture does not lead to two-phase microstructure and simply plastisizing effect is observed. The two-phase microstructure was obtained by using prepolymer of epoxidized soybean oil (ESO) and amine hardener instead of pure ESO. The high molecular weight of the prepolymer compared to pure ESO reduces the compatibility with epoxy and favors phase separation. The effect of ESO content on impact properties of modified networks made by both one-stage and two-stage process, as reported by Ratna *et al.*⁴⁹ is shown in Figure 4. Significant increase in impact strength was observed for the blends made by two-stage process and the optimum modifier concentration

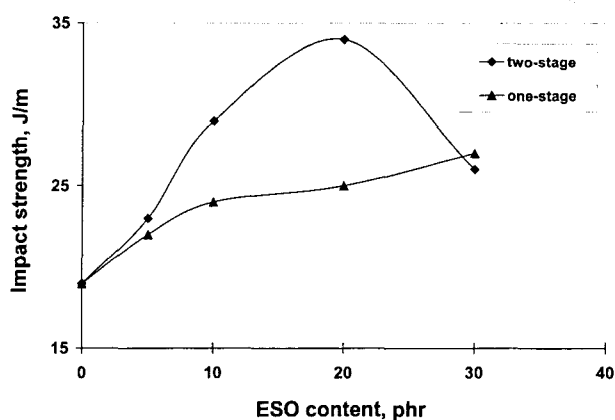


Figure 4. Effect of ESO content on impact strength of toughened epoxy network.

in terms of toughening was found to be 20 phr (phr stands for parts per hundred grams of epoxy resin). Above 30 phr of rubber concentration phase inversion occurs.^{48,49}

Saturated Liquid Rubbers

The liquid rubber like carboxyl terminated copolymer of acrylonitrile and butadiene i.e. CTBN toughened epoxy often shows outstanding fracture properties and the technology is exploited in the field of engineering adhesives.⁵⁰ However, since the butadiene component of the elastomer contains unsaturation, it would appear to be a site for premature thermal and/or oxidative instability and such modified resins are not suitable for application at high temperature.⁵¹ One would imagine that excessive crosslinking could take place with time which would detract from otherwise desirable improvements accomplished with these structures. Secondly, there is some limitation in its use due to possibility of the presence of traces of free acrylonitrile, which is carcinogenic.⁵² Hence, considerable efforts have been made, in the last two decades, to develop saturated liquid rubber alternative to CTBN.

Siloxane rubbers, because of their attractive properties like high chain flexibility, extremely low T_g ($\sim -100^\circ\text{C}$), low surface tension and surface energy and hydrophobic behavior has been investigated as the toughening agent. Poly(dimethyl siloxane) oligomer (PDMS) can not be used as such, because of its extreme incompatibility with epoxy. The compatibility is increased by copolymerizing dimethyl siloxane with diphenyl siloxane or dimethyl fluoropropylsiloxane.⁵³ Such copolymer having controlled structure can be successfully used as toughening agents.⁵³⁻⁵⁵ Konzol *et al.*⁵⁶ have reported that the miscibility of PDMS can be increased by introducing polycaprolactam (PCL) block into PDMS. Hydroxyl-terminated block copolymers having basic structure $(\text{PCL})_2$ -*b*-PDMS-*b*-(PCL)₂ with controlled composition leads to phase separated system with uniformly dispersed elastomeric particles in the order of magnitude of 20 nm.⁵⁷ Incorporation of about 5% of such modifier resulted in the two-fold increase in toughness.^{56,57} Recently Tog *et al.*^{58,59} showed that the miscibility of PDMS with epoxy can be improved by grafting the PDMS with glycidyl methacrylate (GMA). The graft segments of PMMA and PGMA on the surfaces of siloxane particles enhance their compatibility with the epoxy and ensure homogeneous distribution of particles leading to an effective toughening effect.

Riffle *et al.*^{60,61} developed an epoxy-terminated siloxane oligomer and used successfully for the toughening of epoxy resin. The epoxy-terminated oligomer was further reacted with piperazine to get secondary amine group end capped oligomer and the same has also been used as toughening agent for epoxy. Silicone-epoxy block copolymers have also been reported⁶² as toughening agent for epoxy. Lanzetta *et al.*⁶³ have modified epoxy resin by hydroxyl-terminated block

copolymers of PDMS and polyoxyethylene (PDMS-*co*-PEO) elastomer and functionalized saturated polybutene. These modified networks exhibit better oxidative stability but do not produce effects reported in the literature for CTBN and ATBN on the mechanical properties of epoxy.

Polyepichlorohydrin (PECH) is reported as a toughening agent for epoxy in the literature.⁶⁴ The structure of PECH, with its pendent chloromethyl groups and terminal hydroxyl groups, gives great flexibility in the variation of interactions that could be introduced either by prereaction or curing reaction. The degree of toughening depends on the molecular weight of the PECH and on the curing temperature. Best toughness was achieved with PECH of highest molecular weight of 3,400 g/mol. The effect of incorporation of PECH rubber on the matrix properties like T_g , modulus, hot/wet properties is similar to that of CTBN rubber.

Carboxyl-terminated poly(propylene glycol) adipate (CTPPGA) has been used as a liquid rubber for the development of an ambient temperature curing epoxy adhesive.⁶⁵ The effect of molecular weight of liquid rubber and concentration of rubber added, on the adhesive strength has been investigated. It was reported that for effective toughening the molecular weight must be above 5,000 g/mol and the addition of 15 phr of such CTPPGA resulted in the three-fold increase in lap shear strength and five-fold increase in T-peel strength. The improvement is comparable to that what achieved by using CTBN.^{65,66}

Recently polyurethane (PU) oligomer has been investigated as a modifier for epoxy by Wang and Chen.⁶⁷ They developed hydroxyl, amine and anhydride terminated PU prepolymer by reacting the isocyanate ended PU oligomer with bisphenol A, diamino-diphenyl sulfone (DDS), and benzophenone tetracarboxylic anhydride respectively. On evaluating the oligomers having different reactive groups as toughening agent for epoxy they found that hydroxyl terminated oligomers perform the best and the incorporation of about 20% of this oligomer into epoxy matrix resulted in five fold increase in fracture energy compared to the unmodified epoxy.

Laeuger *et al.*⁶⁸ have reported the toughening of anhydride cured DGEBA resin by using diol and bis(4-hydroxy benzoate) terminated poly(tetrahydrofuran) liquid rubber. The morphology development occurs via spinodal decomposition and monitored by Transmission Electron Microscopy (TEM) and small angle light scattering. The liquid rubbers react with DGEBA to form segmented liquid rubbers with poly(tetrahydrofuran) and poly(hydroxy ether) segments. The bis(4-hydroxy benzoate) terminated poly(tetrahydrofuran) gives better performance compared to the diol terminated one as far as mechanical and fracture properties are concerned.

Wang *et al.*⁶⁹ have synthesized polyfunctional poly(*n*-butyl acrylates) (containing epoxy and carboxyl group) by photopolymerization and used to toughen epoxy resin cured with diamino diphenyl methane (DDM). They found that there is an optimum functionality for maximum impact

resistance epoxy and carboxyl functionalized and epoxy functionalized liquid rubber modified systems. Lee and coworkers⁷⁰ obtained similar results using *n*-butyl acrylate/acrylic acid copolymers. They reported that improvement of adhesion strength could be achieved by incorporating the *n*BA/AA copolymer in a DGEBA epoxy matrix and that an optimum functionality existed to achieve the highest interfacial adhesion.

Banthia *et al.*⁷¹ have shown that carboxyl-terminated poly (2-ethyl hexyl acrylate) (CTPEHA) oligomer is superior to other acrylic rubber in terms of solubility parameter. They have studied the kinetics of bulk polymerization of different monomers and found the minimum heat of reaction for 2-ethyl hexyl acrylate monomer. Ratna *et al.*^{72,73} have synthesized a series of CTPEHA oligomers by bulk polymerization having different molecular weights. The carboxyl functionality (*f*) of the liquid rubbers were in the range of 1.7 to 1.9 eq/mol. The effect of molecular weight on toughening is shown in Figure 5. The liquid rubbers having number average molecular weight in the range of 3,000-7,000 g/mol behave almost equally and the toughening effect decreases with further increase in molecular weight. Incorporation of 10 phr of CTPEHA oligomer ($M_n < 7,000$ g/mole) into epoxy matrix resulted in a two-fold enhancement in impact strength.

Iijima *et al.*^{74,75} used an acrylic elastomer containing pendent epoxy groups to reduce the brittleness of DGEBA resin cured with DDS. The elastomers were prepared by copolymerization of butyl acrylate (BA), vinyl benzyl glycidyl ether (VBGE) and styrene (St) or acrylonitrile. The addition of 20% of the terpolymer (74 mole% BA, 18 mole% VBGE and 8 mole% St) resulted in an 80% increase in fracture energy of the cured resin at the slight expense of its mechanical properties.

Very recently, a new class of reactive liquid rubbers which are dendritic hyperbranched polymers (HBPs) has been investigated as a modifier for epoxy resin.⁷⁶⁻⁷⁹ The advantages of HBPs over the conventional toughening agents are that HBPs offer much lower prepolymer viscosity because of

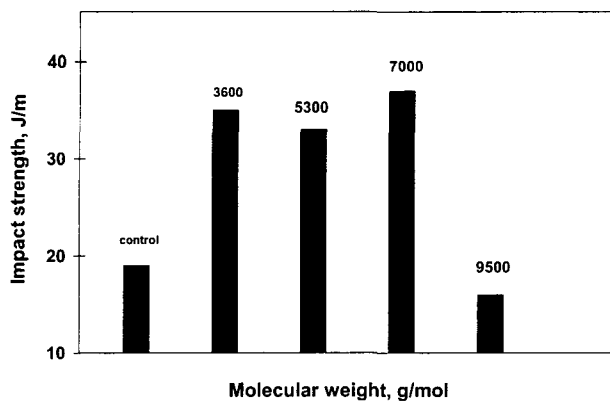


Figure 5. Effect of molecular weight of CTPEHA on impact behavior.

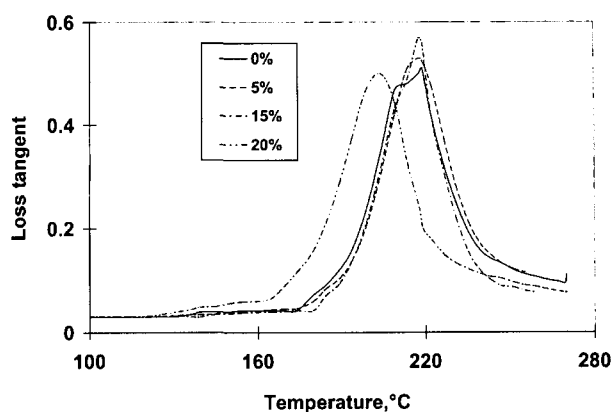


Figure 6. Loss factor vs. temperature plots of epoxy/HBP blends.

their spherical structure and better internal bonding and stronger adhesion with the matrix due to the presence of a high density of surface functional groups. Boogh *et al.*⁷⁶ reported increase in critical strain energy release rate (G_{ic}) by a factor of 6 as re-result of incorporation of 5% of epoxy functionalized HBP in the epoxy matrix. The dynamic mechanical properties of DGEBA/HBP blends as shown in Figure 6, reported by Ratna *et al.*,⁷⁸ indicates complete phase separation up to 15 phr of HBP concentration.

The performance of some new liquid rubbers and CTBN modified DGEBA epoxy was summarized in Table II.

Toughening by Preformed Particle

The phase separation, in case of liquid rubber toughening depends upon the formulation, processing and curing conditions. Incomplete phase separation can result in a significant lowering of glass transition temperature (T_g). Moreover, the rubber phase that separates during cure is difficult to control and may result in uneven particle size. The differences in morphology and volume of the separated phase affect the mechanical performance of the product. The factors that affect the fracture toughness of the modified epoxy such as morphology, particle size and composition are interdependent, hence it is very difficult to study the effect of individual parameter. These problems can be minimized by using insoluble preformed particle directly.⁸⁰⁻⁸⁴ Since the size, morphology and composition, shell thickness and crosslink density of the rubbery cores can be controlled separately by employing emulsion polymerization techniques, the effects of various parameters on the toughening of epoxies can be investigated. The control of the particle parameters by emulsion polymerization has been extensively studied, and various efficient technologies have been developed.⁸⁵⁻⁸⁹ Monodisperse latex particles with a diameter from submicron to micron range can be prepared by sequential seeded emulsion polymerization,⁸¹ sequential swelling process⁸⁶ and dispersion

Table II. Impact Properties of Some Liquid Rubber Toughened Epoxy

Liquid Rubber	Optimum Conc.	Curing Agent	Improvement in Property	Ref.
CTBN	15 phr	HY 960 ^a	400% T-peel strength	66
CTPPGA	15 phr	HY 960 ^a	400% T-peel strength	65
CTPEHA	10 phr	HY 951 ^b	100% impact strength	72, 73
ESR	20 wt%	HY 960 ^a	100% Lap shear strength	48
PECH	10 phr	Piperidine	66% fracture toughness K_q	64
PU prepolymer	not established	DDS	400% fracture energy G_{IC}	67
BA, VBGE, St terpolymer	20 wt%	DDS	80% fracture energy G_{IC}	74, 75
HBP	5 wt%	Isophorondiamine	600% fracture energy G_{IC}	76

^aTris-2,4,6-(*N,N*-dimethyl amino methyl) phenol. ^bTrimethylene tetramine.

polymerization.^{87,88} Cohesive strength, which is influenced by crosslink density of the rubber phase, can be controlled by the conversion of polymerization and the amount of crosslinking agent.⁸⁹ Interfacial architecture can be controlled by changing the following parameters : (1) thickness of the shell which depends on the ratio of the shell-core materials and polymerization mechanism; (2) chemical bonding and physical interaction between particles and matrix which can be enhanced by introducing functional groups onto the surface of the shell; (3) grafting between the shell and core and (4) molecular weight of shell materials. Various morphologies of the composite such as core shell, occluded or multilayer can be achieved through two or multiple stage emulsion polymerization.^{90,91} Typically, core shell morphology latex particles can be made by semicontinuous process under a monomer starved condition.⁹²

The preformed particles are incorporated into the epoxy matrix by mechanical mixing. The dispersibility of the particles can be improved by 1) introducing crosslink into the shell or 2) using comonomer like acrylonitrile or glycidyl methacrylate (GMA) which increases the interfacial adhesion by polar or chemical interaction.^{93,94} Quan *et al.*⁹⁵ have reported that in case of poly(butadiene-*co*-styrene) core poly(methyl methacrylate) (PMMA) shell particles, the cluster size reduces from 3-5 μ m to 1-3 μ m as a result in the use of 5% crosslinker (divinyl benzene). They also found that the cluster size could be further reduced to 1-2 μ m by using MMA-AN or MMA-GMA copolymer as shell composition.

Lin *et al.*^{96,97} have prepared reactive core shell particles (CSPs) with butyl acrylate as core and MMA-GMA copolymer as shell and used them as toughening agents for DGEBA epoxy. They found that shell crosslinked CSPs had higher toughening effect than core crosslinked CSPs. They also reported tremendous effect of comonomer like GMA on the toughening effect. This seemed to contradict with Sue's observation that chemical bonding of CSP to the epoxy matrix did not significantly contribute to the toughening performance.⁹⁴

Matrix Ductility and Toughening

The most accepted mechanism for rubber toughening is rubber cavitation followed by shear yielding.⁹⁸⁻¹⁰³ The role of rubber particles is to cavitate internally, thereby relieving the hydrostatic tension and initiating the ductile shear yielding mechanism.^{98,99} The toughening mechanism highlights the role of inherent ductility of the matrix in influencing the toughness of multiphase network. For example, a decrease in the stress needed for localized shear yielding should obviously assist in increasing the toughness if all other microstructural features are unchanged.^{104,105} Rubber toughening of the brittle tetraglycidyl methylene dianiline (TGMDA) based networks have resulted in minimum improvement of fracture energy in contrast to the comparatively ductile DGEBA based networks^{106,107}

The ductility of the matrix can be increased by introducing flexible linkage^{108,109} into the rigid backbone or by reducing the cross-link density i.e. by increasing the molecular weight between crosslinks (M_c).¹⁰⁹⁻¹¹¹ The effect of M_c on the fracture energy is more observed in rubber toughened epoxy compared to the unmodified epoxy. Pearson and Yee¹¹² studied the toughness of a series of epoxy-CTBN polymers cured with DDS. The M_c in this series was varied by using epoxy resin of different epoxy equivalent weight ; the higher is the epoxy equivalent the higher is the subsequent value M_c . They found that an increase in M_c produces a small increase in the value of fracture energy for unmodified polymers and a dramatic increase in fracture energy for rubber toughened polymers. The similar type of observation was reported by Finch *et al.*¹¹³ and Levita *et al.*¹¹⁴. They varied the M_c in the epoxy matrix of an epoxy-CTBN system that was cured with piperidine by changing the cure time and temperature. The microstructure of the dispersed particles in the modified materials was not found to be significantly changed by different curing reaction.

Lavita *et al.*¹¹⁵ has plotted the fracture energy of toughened thermoset vs. the fracture energy of the unmodified epoxy

which represents an amplification factor of 10. TGMDA based resin formulation cured with PIP are more amenable to toughening by addition of CTBN than the DDS hardened system because of the lower ductility of the latter.¹¹⁶ The fracture energy of TGMDA-PIP is 4 times greater than that of TGMDA-DDS system but fracture energy of CTBN modified (20 phr) TGMDA -PIP system is 24 times greater than that of the toughened TGMDA-DDS system.¹¹⁷ This is because the rubber rich particles as stress concentrator, induce plastic deformation of highly brittle matrix to a far lesser extent.

Microstructural Features

The morphological parameters like rubber volume fraction, particle size and particle size distribution have a major effect on the toughness of multiphase polymer. In many studies, several crucial features have been changed simultaneously. Moreover, different parameters are interrelated and it is difficult to change one parameter without affecting others. However, attempt has been made here to correlate the fracture behavior and microstructural features of the toughened networks based on the available results in the literature.

The fracture energy of toughened epoxy materials increases with increase in volume fraction of rubber. The maximum value of volume fraction can be achieved is about 0.2-0.3.¹¹⁸⁻¹²⁰ Attempts to produce higher volume fraction results in phase inversion and loss of mechanical fracture properties. Though in most of the studies,^{118,119} phase inversion is reported at volume fraction higher than 20%, in some recent studies inversion is reported¹²⁰ at very low volume fraction ($< 5\%$).

Kunz *et al.*^{121,122} have reported that large (40 mm diameter) particles are not efficient in providing an increase in fracture energy as smaller (1 mm) particles. They have incorrectly attributed it to the difference in tearing energy of rubber particles. Many authors^{123,124} reported that fracture energy of rubber toughened epoxy is independent on the particle size. However, the average particle size was only varied between 0.5-5 mm. Pearson and Yee¹²⁵ have studied the effect of particle size on the fracture properties of rubber toughened epoxy network having particle size ranging from 0.2-200 mm. They found that large, 100 mm diameter particles are not as effective in providing a toughening effect whereas small, 0.1 mm diameter particles appear to be the most efficient and provides over a ten fold increase in fracture energy.

The origin of this size dependence arises from the role played by the particles, which is governed by the size of the process zone. Large rubber particles lying outside the process zone are only able to act as bridging particles, which provide only a modest increase in fracture energy. Small rubber particles which lie in the process zone are forced to cavitate by the large hydrostatic stress component that exist in the process zone and contribute to the increase in fracture

energy.

This is also consistent with the notion of interparticle distance concept proposed by Wu¹²⁶ for rubber toughened nylon and extended by Pearson¹²⁷ for rubber toughened epoxy. They argued that there is a critical inter particle distance below which the material is tough and above which the material is brittle. Critical interparticle distance or matrix ligament thickness is the fundamental parameter and does not depend on the rubber volume fraction or particle size. For a fixed volume fraction of rubber the inter particle distance can be reduced by decreasing the particle size.

Other researchers^{128,129} have claimed that the optimal particles size actually involves a bimodal distribution of small and large particles. They reported that rubber modified networks having bimodal distribution of particles exhibit higher fracture toughness than that of the matrix having unimodal distribution of particles. Bimodal distributions were achieved by using bisphenol-A, which also acts as chain extender and improves the toughenability of the matrix. Hence these claims have neglected the effect of crosslink density which has been shown to be quite substantial.¹⁰⁴⁻¹¹³ Moreover Yee and Pearson^{125,130} have disproved the effect of bimodal particle distribution on several morphological scale. They have not found any synergistic effect combining 0.2 mm particles with 2 mm particles and 2 mm particles with 100 mm particles.

Despite the influence of volume fraction, particle size and particle size distribution has been significantly studied the role of morphology in rubber toughened epoxy has not been thoroughly examined. Yamanaka *et al.*^{40b} observed lower yield strength, higher damping capacity and higher peel strength in a rubber toughened epoxy when the blend contained connected microstructure compared to that of a blend with discrete morphology. These researchers therefore concluded that the connected morphology results in an ease of shear yielding which may improve the fracture toughness as well. Parenthetically speaking, no proper means of fracture toughness assessment was employed in their study, which weakens their argument. Sue *et al.*¹³¹ found a modest improvement in the fracture toughness of a DGEBA/DDS system modified by core shell rubber particles when the particles had a connected morphology compared to a well dispersed microstructure. These researchers attributed their observation to the additional toughness provided by crack deflection around the locally clustered particles. Bagheri *et al.*¹³² investigated the effect of the morphology using more ductile DGEBA/piperidine system and found that the fracture toughness of a blend with a connected microstructure is significantly higher than that of similar blend containing uniformly dispersed particles. The reason lies in the fact that the connected morphology enables shear bands to grow further at the crack tip.

Conclusions

From the above review the following conclusions can be

drawn :

1. The epoxy resins can be toughened successfully by blending a small amount (about 10-15% by weight) of liquid rubber or by incorporating the preformed rubbery particles directly. The resulting morphology can be better controlled in case of preformed particle.

2. The improvement of fracture resistance i.e. toughening occurs due to dissipation of mechanical energy by cavitation of rubber particles followed by shear yielding of the matrix.

3. The toughenability of the matrix increases with increase in the inherent ductility of the matrix. Hence, difunctional epoxy resins are more easily toughened by addition of rubber than the tri and tetrafunctional epoxy resins.

4. The rubber particles, having size 0.1 to 5 mm, and uniformly distributed throughout the matrix, can effectively toughen epoxy resin. The particles having size more than 10 mm and haphazardly distributed particles can not result effective toughening.

5. The cocontinuous morphology having some extent of connectivity gives higher toughening effect than the discrete morphology. However, the optimum extent of connectivity is yet to be established.

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