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Effect of cross-linking density on the toughening mechanisms of rubber-modified thermosets

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Solid rubbers have been incorporated into thermosets using the compositional quenching process. Electron micrographs reveal that rubber particles a few micrometres or less in size have been dispersed in the matrix. Two model systems were studied: an epoxy resin cured with primary amines which represents a tight network structure, and a phenoxy resin cross-linked with methylene diisocyanate which represents a loose network. The present study indicates that a small amount of a cross-linking agent can reduce the degree of matrix yielding with a resultant drop in impact strength. SEM fractography provides complementary information on the transition from ductile fracture to brittle fracture.

1. Introduction

The compositional quenching process was patented by Nauman in 1986 [1]. Since that time, our research has spanned a variety of areas related to compositional quenching. The underlying physical process of spinodal decomposition has been studied from a theoretical standpoint [2–5]. Experimental research projects have involved the manufacturing of rubber-modified engineering plastics (ABS [6], polyphenylene ether [6], and polyimides [7]) and thermosets (epoxy resins [6] and phenolic resins [8]). The role of interfacial bonding in the particulate reinforced-composites has been studied using continuum mechanics [9].

Compositional quenching provides a novel method of incorporating rubbers into an otherwise brittle matrix without interfacial bonding. One of the advantages of this process is that the morphology of the final product can be precisely controlled. Fig. 1 presents the morphologies of polymer blends produced by different processes. Phase separation during bulk, suspension and emulsion polymerization generally produces spherical rubber particles with matrix occlusions. Even though such occlusions increase the effective volume of the rubber particles, the yield strength and modulus drop substantially. For example, the yield strength of commercial HIPS is about one-third that of polystyrene [10]. Melt blending tends to disperse the rubber as irregularly-shaped particles. Stress analysis in a review paper by Chow [11] shows that the stress concentration factor increases as the aspect ratio increases. Thus, an irregularly-shaped particle is also undesirable. Compositional quenching yields non-occluded spherical particles well-dispersed in the matrix. Experimental results [6, 7] proved that the rubber-modified thermoplastics gain toughness with limited sacrifices in the yield strength and modulus.

The traditional route to toughen epoxies was pioneered by McGarry and Sultan [12], who used reactive liquid carboxyl-terminated nitrile rubber (CTBN) with a weight average molecular weight about 3000. They observed that a CTBN/epoxy system cured with piperidine improved the fracture toughness ten-fold. Riew *et al.* [13] found that the toughness of the CTBN/epoxy/piperidine system can be further improved by the addition of bisphenol A. Using the compositional quenching process, 5% polybutadiene/epoxy/piperidine system also has improved mechanical properties [6]. However, the significant improvement of impact strength in an epoxy cured by primary amines has not been reported.

The object of this study was to investigate the structure–property relationships of the rubber-modified thermosets. Specifically, we have investigated the effect of cross-linking density on the toughening mechanisms in thermosets. Epoxy resins and a phenoxy

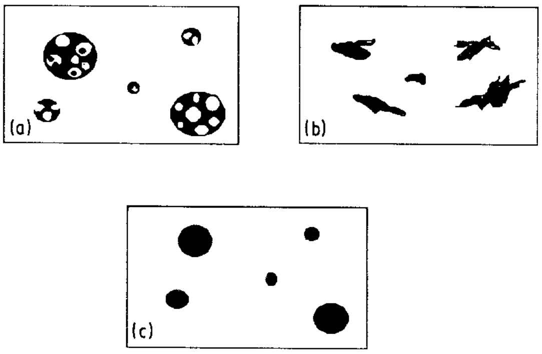

Figure 1 Particles produced by (a) matrix polymerization (b) melt processing and (c) compositional quenching.

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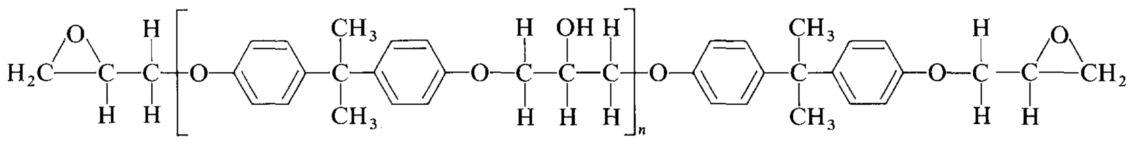


(I)

resin have been selected as model materials because of their similarity in chemical structure. The distinctions between the phenoxy molecular structure and that of conventional epoxy are: (1) phenoxy contains no epoxy group; (2) phenoxy is 10 to 30 times higher in molecular weight; (3) phenoxy requires no curing or chemical reaction to become a useful product; (4) phenoxy has an essentially linear molecular structure [14]. Other information of phenoxy resins can be found in the literature [15–17].

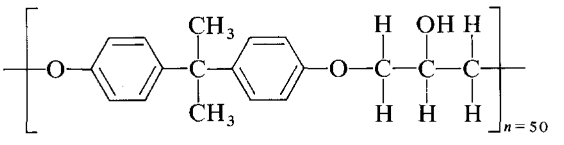
2. Experimental procedure

2.1. Materials

The epoxy resins (Structure I) used in this study result from the reaction of bisphenol A with epichlorohydrin. Epon 828 and Epon 834, epoxy resins obtained from Shell Chemicals, have epoxy equivalent weights of 190 and 250, respectively, and $n = 0$ (86%) and 1 (14%) for Epon 828, and $n = 0$ (29%) and 1 (71%) for Epon 834.

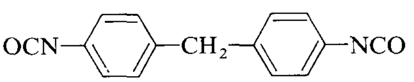
The curing agents for the epoxy resins were metaphenylene diamine (MPDA), Tonox 40/60 (a eutectic mixture of 40% MPDA and 60% 4,4′-methylenedianiline [18]) and diethylene triamines (DETA). The selection of the curing agent was dependent on the viscosities of the final products.

PKHH, (Structure II) a phenoxy provided by Union Carbide Corporation, is a high molecular weight polymer of bisphenol A and epichlorohydrin.



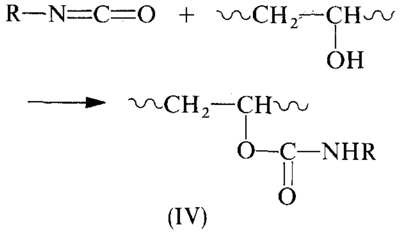
(II)

Phenoxy resins can be cross-linked with polyisocyanates, urea, phenol or melamine formaldehyde resins through the secondary hydroxy groups to yield excellent solvent resistance. The cross-linking agent used in this study was Rubinate 44, a highly pure difunctional methylene diphenyl diisocyanate (MDI, Structure III), ICI Americas Inc. The isocyanate equivalent weight is 125 and the melting point is 38 °C.



(III)

Isocyanates react with phenoxy resins via the hydroxyl group yielding a urethane linkage. A cross-linked system (Structure IV) is obtained from this difunctional material and the polyols of phenoxy resins [19].



$$R{-}N{=}C{=}O + \sim CH_2{-}\underset{OH}{CH}\sim \longrightarrow \sim CH_2{-}\underset{O-\underset{O}{\overset{\|}{C}}-NHR}{CH}\sim$$

(IV)

A polybutadiene and/or a nitrile rubber were used in this study. Polybutadiene tends to agglomerate at high concentrations during the compositional quenching process whereas a nitrile rubber may form a single-phase mixture with epoxy resins owing to their compatibilities. Taktene 1202 and Hycar 1042 nitrile rubber were employed in this study.

Taktene 1202, a rubber with high *cis*-1,4-polybutadiene content, was obtained from Polysar Incorporated. The glass transition temperature is − 110 °C, one of the lowest of the rubbery polymers. The weight average and number average molecular weights are 375 000 and 114 600, respectively [20].

Hycar 1042, a random copolymer of acrylonitrile and butadiene with 31% acrylonitrile content, was provided by BF Goodrich Company. The glass transition temperatures of this elastomer are − 38 and − 24 °C [21]. The weight average molecular weight is approximately 400 000.

2.2. Mixture preparation

In order to obtain uniformly dispersed rubber particles of definite size and shape in the final product, rubber selection is much more restrictive in epoxy resins than in phenoxy resins. The viscosity of epoxy resin is low and decreases dramatically as the temperature increases, while the viscosity of the phenoxy resin is relatively insensitive to temperature. Phase coarsening tends to occur in the compositional quenching process or during curing if the rubber, such as polybutadiene, is not compatible with the epoxy resin. If the rubber, such as nitrile rubber, is compatible with epoxy, the high viscosity of the rubber–epoxy mixture results in processing difficulties such as mould filling and degassing during cure.

Table I presents the compositions of the specimens of nitrile rubber-modified epoxy systems. Systems containing over 15% Hycar 1042 nitrile rubber had high viscosities and required high mixing and degassing temperatures. Instead of Epon 834, the lower viscosity Epon 828 was used. Tonox 40/60 was selected over MPDA because the former is less reactive.

To reduce the difficulty of processing, a mixed rubber/epoxy system, which has a low viscosity, was made. One part of a nitrile rubber with two parts of a

TABLE I Izod impact strength of nitrile rubber-modified epoxy resins

Epoxy resins	Rubber content (%)	Curing agent	Stoichiometric ratio	Izod impact (ft lb in^{-1})^a
Epon 834	0	MPDA	1:1	1.79
Epon 834	7% Hycar 1042	MPDA	1:1	1.01
Epon 834	7% CTBN	MPDA	1:1	1.10
Epon 834	10% Hycar 1042	MPDA	1:1	0.75
Epon 828	0	Tonox 40/60	1:1	0.91
Epon 828	10% Hycar 1042	Tonox 40/60	1:1	0.65
Epon 828	15% Hycar 1042	Tonox 40/60	1:1	0.70

^{a} 1 ft lb in^{-1} = 53.38 × 10^{-3} J mm^{-1}

polybutadiene rubber were found to control successfully the morphology of the rubber-modified epoxy. Table II presents such a mixed rubber/epoxy system. For comparison, the same mixed rubber compositions were used in the phenoxy system, Table III.

TABLE II Compositions of the mixed rubber/Epon 828 system

Sample	Rubber content (%)	Composition (wt %) NR/PB/Epon 828
1	0	0/0/100
2	5	1.67/3.33/95
3	10	3.33/6.67/90
4	15	5/10/85
5	20	6.67/13.33/80

TABLE III Compositions of the mixed rubber/phenoxy (PKHH)* system

Sample	Rubber content (%)	Composition (wt %) NR/PB/PKHH
1	0	0/0/100
2	10	3.33/6.67/9
3	15	5/10/85
4	10	6.67/13.33/80
5	25	8.33/16.67/75

The compositional quenching process, as shown in Fig. 2, was used to incorporate elastomers into epoxy and phenoxy resins. In the epoxy system, a nitrile rubber (or a mixture of one part of nitrile rubber and two parts of PB rubber) and an epoxy resin were dissolved in a common solvent (THF), by mechanical mixing. This solution was then heated to 260 °C and pressurized to 500–1000 p.s.i. (10^3 p.s.i. = 6.89 N mm^{-2}) to prevent boiling in the heat exchanger. THF was removed when this solution entered the flash chamber which was maintained at 5 torr (6.665×10^2 Pa). The temperature was about 210 °C before entering the flash chamber. The final blend was a single-phase mixture of Hycar 1042 and epoxy. For the mixed elastomer systems, a two-phase mixture was obtained. For the case of phenoxy, the mixed elastomers and the phenoxy resin were dissolved in a solvent consisting of 40% toluene and 60% THF. The operating conditions were exactly the same as in the epoxy system. The final blend was an opaque, two-phase mixture. The total polymer concentrations of the solutions prior to the flash were 10% and 4% for the epoxy and phenoxy systems, respectively.

2.3. Fabrication of the specimen

For thorough cross-linking, the hydrogens of the primary and secondary amines should be matched 1 : 1 with the epoxy group. The amounts of the curing agent and epoxy resin needed in order to obtain the 1 : 1 stoichiometric quantity are calculated as follows from Equation 1.

$$\frac{\text{Molecular weight of amine} \times \text{epoxy equivalent weight (EEW)}}{\text{No. of available hydrogens per molecule} \times 100} = \begin{array}{l}\text{Parts by weight of amine to be used}\\ \text{with 100 parts by weight of epoxy}\end{array} \quad (1)$$

The following general method was used for curing both solid and liquid rubber/epoxy systems.

1. The stoichiometric amount of a primary curing agent was mixed into the rubber/epoxy blend, using a high shear stirrer under vacuum. If necessary, this blend was heated to lower the viscosity.

2. This mixture was poured into an aluminium mould treated with a silicone release agent.

3. The curing schedules were 2 h at 80 °C, 4 h at 150 °C for aromatic amines; 4 h at 40 °C and 12 h at 65 °C for aliphatic amine.

4. On completion of the cure cycle, the heater was switched off and the mould was allowed to cool slowly to minimize residual stress

5. Specimens were machined to specific dimensions for tensile and Izod impact tests.

The heating and cooling rates were 10 and 1 °C min^{-1}, respectively.

The phenoxy resin was dried (6 h in vacuum at 70 °C) and then stored in a container with desiccant before processing. MDI was stored in a freezer (− 20 °C) to prevent dimerization of isocyanate.

All phenoxy samples without MDI were fabricated into tensile and Izod specimens using an air-operated Mini-Jector, an injection moulding machine (Newbury Industries, Inc). The temperature and pressure conditions maintained were 270 °C and 5000 p.s.i., respectively.

Phenoxy/MDI cross-linked systems were manufactured using a male–female compression mould. Moulding conditions were 2000 p.s.i. at 180 °C for 10 min

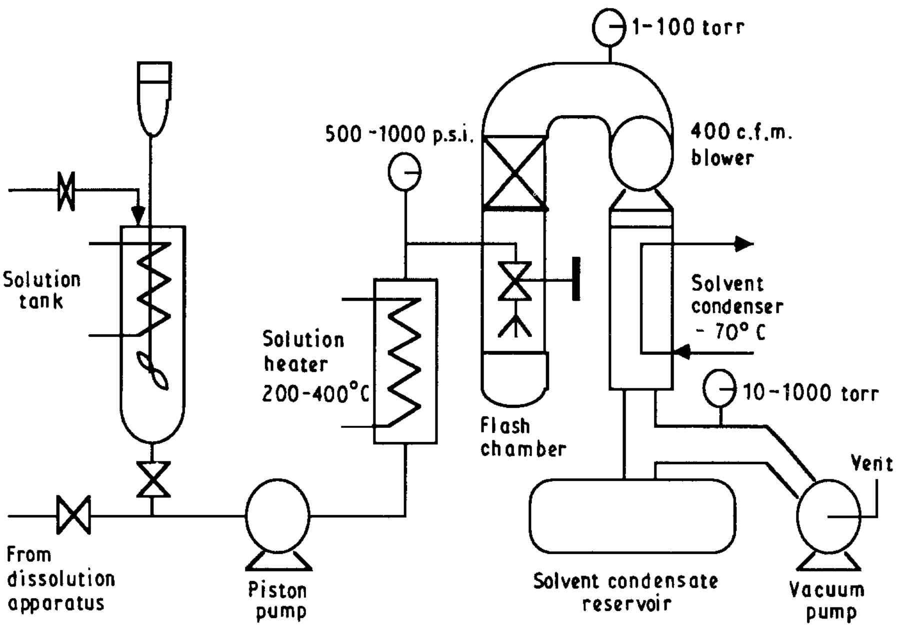


Figure 2 Compositional quenching apparatus.

followed by cooling to 60 °C in the mould. The specimens were machined to the same dimensions as the ones made by injection moulding.

The gauge dimensions of the tensile specimens for the epoxy and phenoxy systems were 2.5 in × 0.5 in × 0.125 in and 0.5 in × 0.125 in × 0.125 in (6.35 cm × 1.27 cm × 0.318 cm and 1.27 cm × 0.318 cm × 0.318 cm), respectively. The strain rate was 0.004 min^{-1} for the tensile test. Owing to the limitation imposed by injection moulding conditions, smaller tensile specimens were used in the phenoxy system. The Izod impact specimens were 2.5 in × 0.5 in × 0.125 in (6.35 cm × 1.27 cm × 0.318 cm) for both systems.

3. Results

3.1. Nitrile rubber-modified epoxies

Nitrile rubber with 31% acrylonitrile content has been found to be compatible with liquid epoxies. Owing to the high viscosity of this single-phase mixture, mixing of the curing agent and degassing had to be conducted at an elevated temperature (typically, 60–90 °C). At such high temperatures, aliphatic amines caused the material to gel before mixing and degassing were completed. Instead, the less reactive aromatic amines (MPDA and Tonox 40/60) were used as curing agents.

During the cure, the nitrile rubber precipitates in the form of spherical rubber domains dispersed in the epoxy matrix. Phase separation is caused by both the increase in molecular weight of the epoxy and the generation of hydroxyl groups along the backbones of the chain. These hydroxyl groups reduce the compatibility of the epoxy with the rubber [22].

Table I summarizes the results of experiments undertaken with a view towards exploring the toughness of nitrile rubber-modified epoxies. The impact strength of rubber-modified epoxy resins is less than that of the control samples. Comparison of Hycar 1042/epoxy/MPDA and reactive liquid CTBN/epoxy/MPDA systems shows the difference in impact strength is insignificant. This observation indicates that chemical bonding does not play a significant role in toughening epoxies. The discussion of the importance of interfacial bonding for different inclusions can be found in the literature [9].

Figs 3–5 are SEM fractographs of impact test specimens. Even though morphologies may be varied with different systems, the average rubber particle size is about a micrometre or less. No debonding between the rubber and the epoxy matrix has been observed.

3.2. Mixed rubber/epoxy/DETA system

Table II presents the compositions of the mixed rubber–epoxy systems that were studied. The effect of the mixed rubber content on the impact strength of the DETA-cured epoxy is shown in Fig. 6. The Izod impact strength is seen to decrease as the rubber content increases. Fig. 7 demonstrates that as the rubber content increases, the yield strength and modulus also decrease.

SEM fractographs of the mixed rubber/epoxy systems are shown in Figs 8 and 9. Most rubber particles are of submicrometre size and are well distributed through the matrix. An improper ratio of nitrile rubber to polybutadiene rubber results in a poor morphology as shown in Fig. 10. The large rubber particles may have resulted from the agglomeration of polybutadiene.

In the rigid three-dimensional network of primary amine-cured epoxies, the rubber inclusions act as stress concentrators. Instead of microshear band formation, microcracks initiate from the rubber particles. In the absence of matrix yielding, these microcracks accelerate the crack propagation and result in poorer tensile and impact properties.

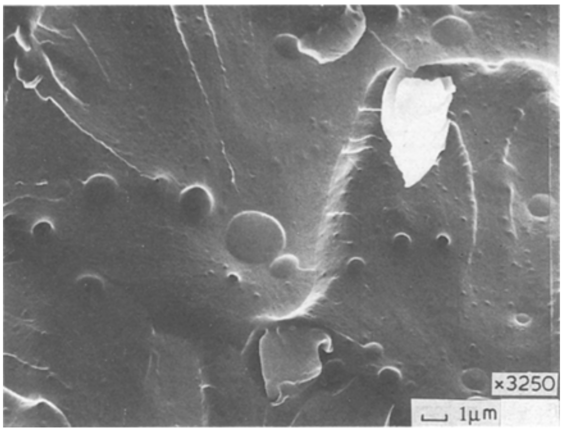


Figure 3 Fracture surface of nitrile rubber-modified epoxy resin.

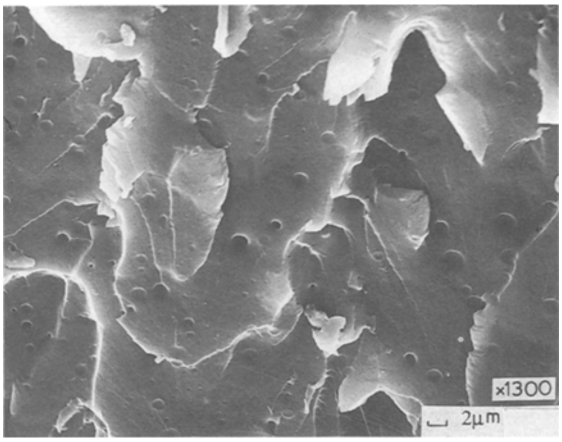


Figure 4 Fracture surface of nitrile rubber-modified epoxy resin.

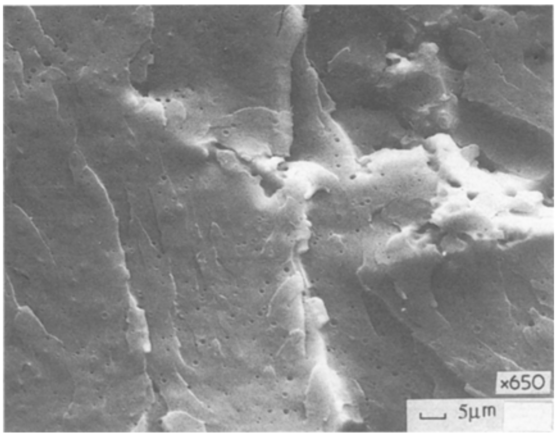


Figure 5 Fracture surface of nitrile rubber-modified epoxy resin.

3.3. Mixed rubber/phenoxy system

The load–displacement diagram of pure phenoxy is presented in Fig. 11. Shear yielding (necking) starts from an internal flaw or surface defect and extends throughout the whole gauge section. Unstable crack growth from such defects result in a scatter in the ultimate strains from 10% to 50%.

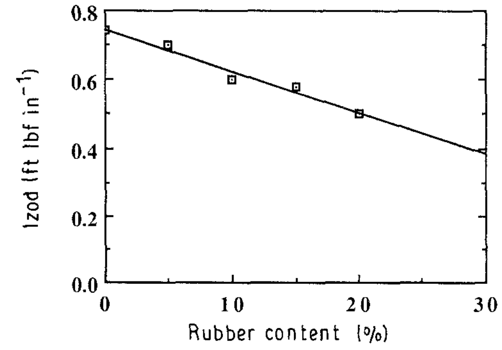


Figure 6 Impact strength of mixed rubber-epoxy system.

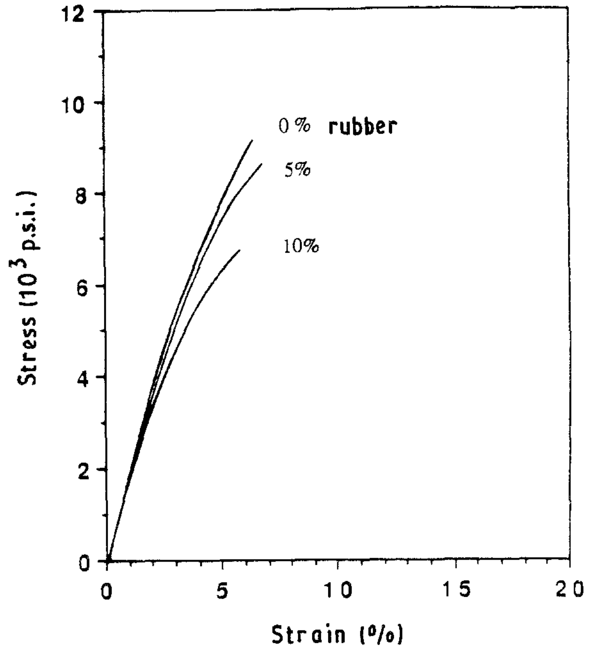


Figure 7 Tensile behaviour of mixed rubber-epoxy system.

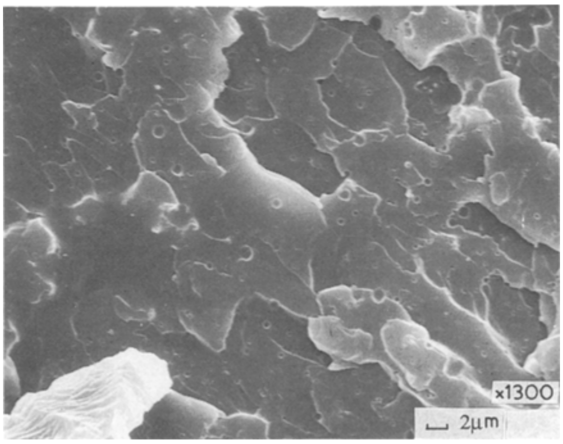


Figure 8 Fracture surface of mixed rubber-epoxy system.

Load–displacement curves of 10%, 15%, 20% and 25% rubber-modified phenoxy are presented in Fig. 12. At low stress or strain states, all the materials follow Hooke's law. Stress whitening and shear yielding occur when the stress reaches the upper yield

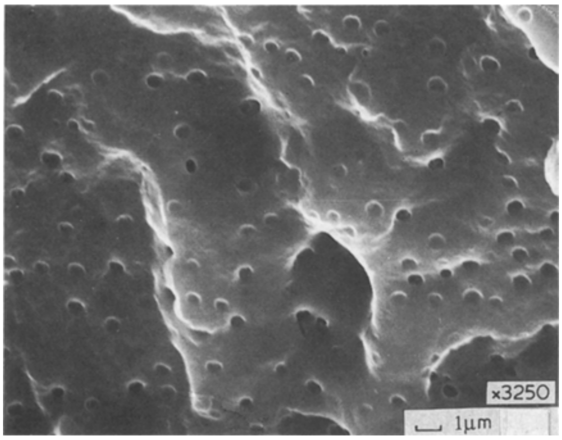


Figure 9 Fracture surface of mixed rubber-epoxy system.

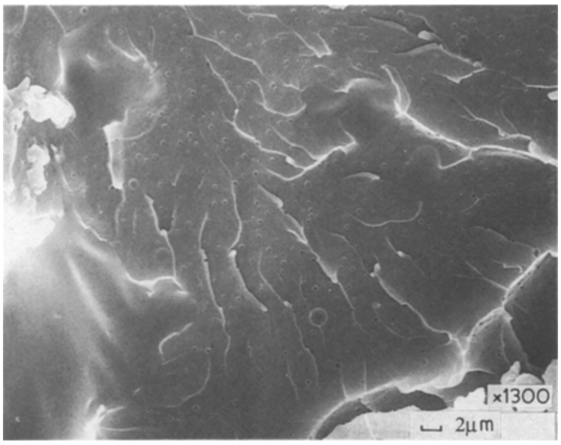


Figure 10 Fracture surface of mixed rubber-epoxy system with excess polybutadiene.

stress. Extensive matrix yielding and molecular orientation during the yield process results in a substantially increased yield strain and ultimate strength for the 10% rubber/phenoxy system. As the rubber concentration increases, the average interparticle distance decreases. This reduced distance results in stress field interactions among the rubber particles. These interactions promote yielding and reduce the modulus, yield strength and failure strain. The magnitude and the percentage change of these properties as a function of rubber content are shown in Figs 13–15.

With the addition of rubber, microshear bands initiate from rubber inclusions and this results in uniform matrix yielding throughout the specimen. Figure 16 schematically illustrates the fracture development processes for neat and rubber-modified phenoxy resins. Rubber inclusions may act as crack arrestors thus preventing catastrophic failure.

The effect of rubber content on the impact toughness of phenoxy resins is shown in Fig. 17. The toughening effect of the rubber inclusions increases initially very rapidly with increasing rubber concentration. The impact strength of the modified phenoxy reaches a maximum, and then begins to decrease with further a increase in rubber content. The initial increase in

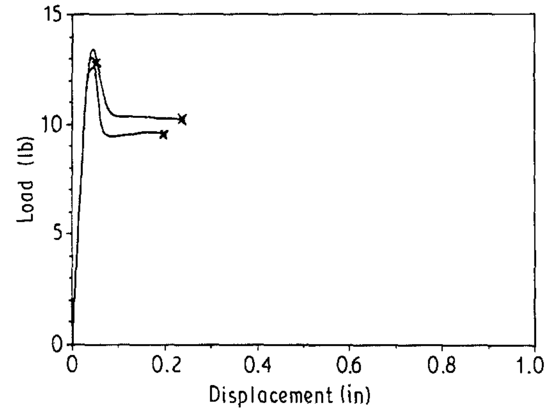


Figure 11 Tensile behaviour of phenoxy.

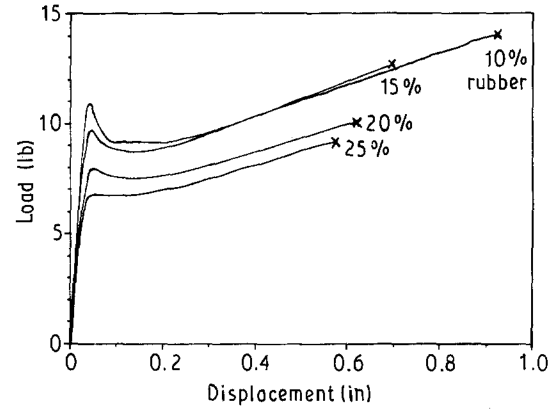


Figure 12 Tensile behaviour of rubber-modified phenoxy.

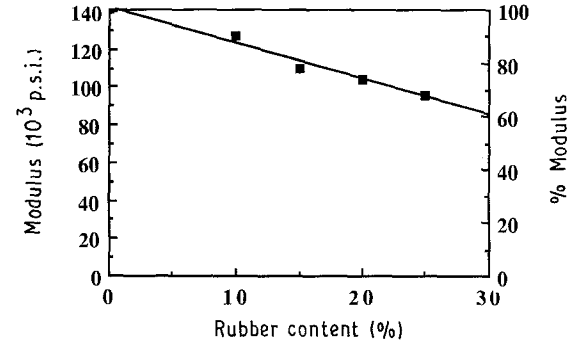


Figure 13 Tensile modulus of rubber-modified phenoxy systems.

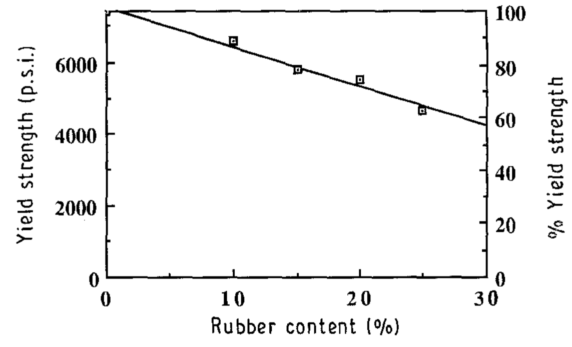


Figure 14 Yield strength of rubber-modified phenoxy systems.

impact toughness with increasing rubber content is due to the presence of more rubber particles which act as nucleation sites for matrix yielding. However, beyond a certain rubber content (in this case 20%), the decrease in impact toughness with increasing rubber content is closely related to the morphology of the sample. At high concentrations, the rubber particles begin to agglomerate, thus decreasing the effective surface area density. At the same time, the interparticle distance is reduced and hence the effective volume of the matrix which undergoes yielding is reduced.

3.4. Effect of cross-link density on the rubber-modified phenoxy resins

Hydroxyl groups attached to the backbone of the phenoxy resin provide the cross-linking sites. Methylene diisocyanate which has difunctional isocyanate groups was selected to cross-link the 10% rubber-modified phenoxy samples. Table IV shows the theoretical M_c (molecular weight between cross-links) of different weight ratios of MDI/phenoxy. The equivalent isocyanate weight of MDI is 125 and the equivalent hydroxy weight of phenoxy is 284.

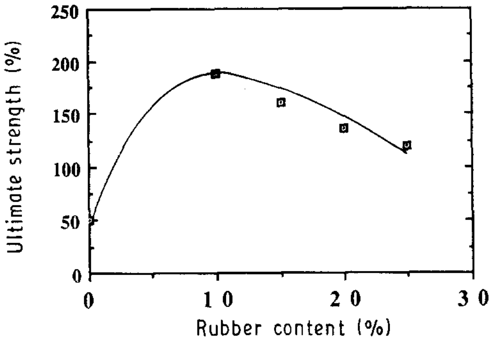


Figure 15 Ultimate strength of rubber-modified phenoxy systems.

The effect of the MDI concentration on the impact strength of rubber-modified phenoxy resin is shown in Fig. 18. For comparison purposes, the 0% and 5.5% MDI-cross-linked pure phenoxy points are also included. The results indicate that even with small amounts of MDI, the impact strength drops substantially. Only at MDI concentrations below 2% is a sharp upturn in impact strength seen. Figs 19 and 20 are the SEM fractographs of the 11% and 1.375% MDI samples, respectively. The brittle fracture surface of 11% MDI sample and the limited plastic deformation of the 1.375% MDI sample result in low impact toughness. Figs 21 and 22 present the fracture surface of the 10% and 20% rubber-modified specimens without MDI. Extensive plastic deformation around the rubber particles accounts for the high impact strength of rubber-modified phenoxy resins. The transition from brittle to extensive plastic deformation is clearly revealed.

To study the homogeneity of MDI in the phenoxy resin, polarized light microscopy was used to study MDI-cured samples. Such samples were microtomed to approximately a 5 μm thickness and placed between two glass plates. Figure 23 shows a micrograph of the 5.5% MDI-cured 10% rubber/phenoxy specimen. It shows that the sample is well-mixed and no cluster of MDI crystals are seen to diffract the polarized light.

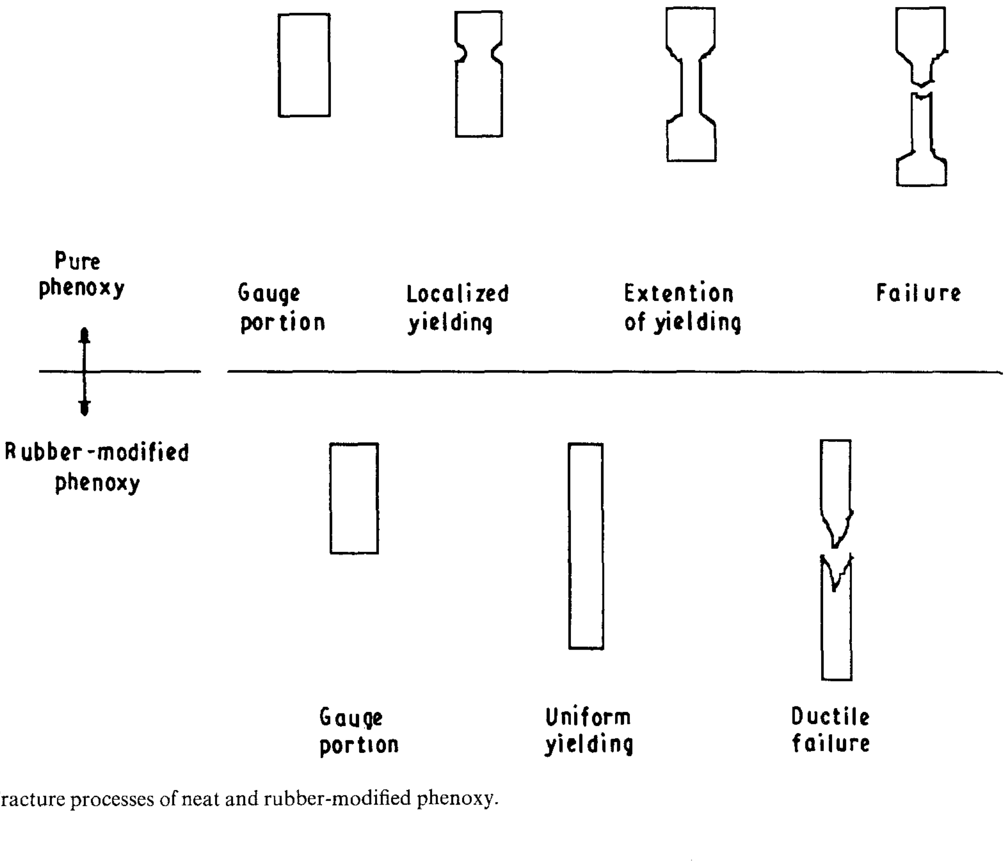


Figure 16 Fracture processes of neat and rubber-modified phenoxy.

TABLE IV Theoretical M_c of different MDI/phenoxy ratio

Phenoxy (parts)	MDI (parts)	M_c
100	44	284
100	22	568
100	11	1136
100	5.5	2272
100	2.75	4544
100	1.375	9088

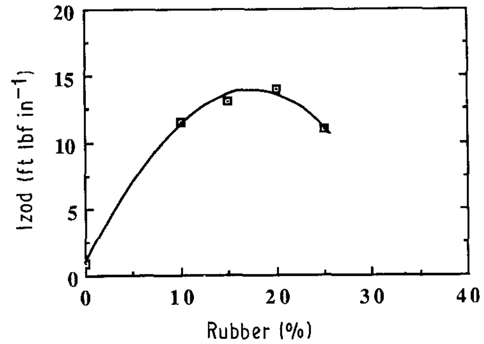


Figure 17 Impact strength of rubber-modified phenoxy systems.

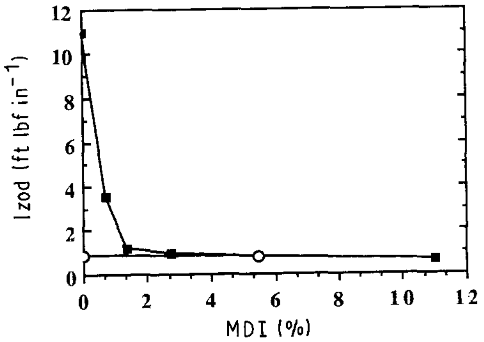


Figure 18 Impact strength of crosslinked rubber-modified phenoxy.

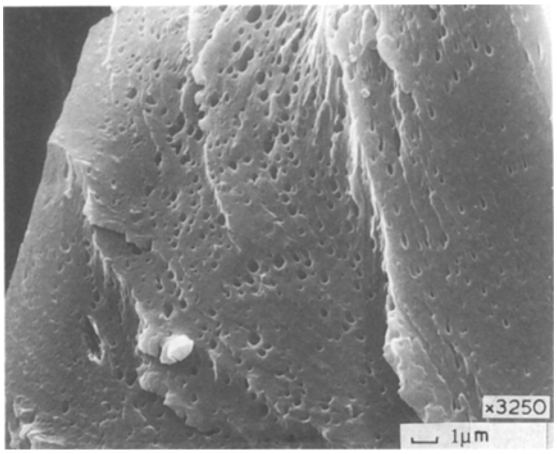


Figure 19 Fracture structure of cross-linked, rubber modified phenoxy, 11% MDI.

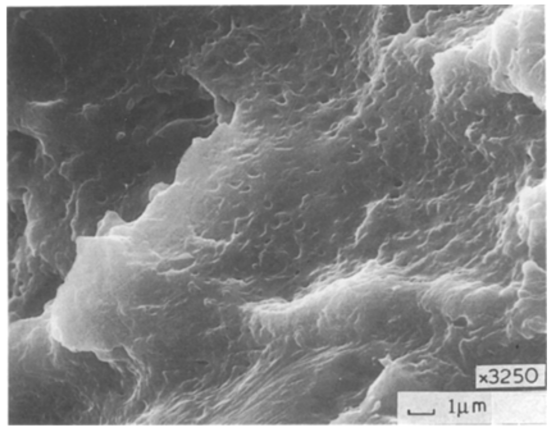


Figure 20 Fracture surface of crosslinked, rubber modified phenoxy, 1.4% MDI.

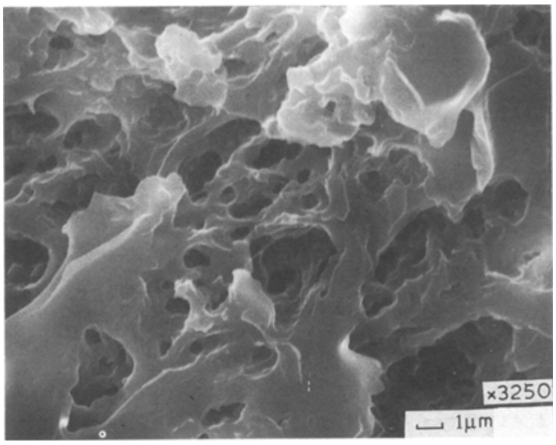


Figure 21 Fracture surface of uncrosslinked 10% rubber-modified phenoxy

4. Discussion and conclusions

To understand the toughening mechanisms of thermosets, two model materials (an epoxy resin and a phenoxy resin) were systematically studied. Epoxy resins cured with primary amines form a tight, three-dimensional network. Segmental movement is severely restricted by the chemical linkages. Phenoxy resins have a structure similar to epoxy resins but are thermoplastic. To control the morphology of the rubber-modified epoxy and phenoxy resins, a nitrile rubber or a mixture of nitrile rubber and polybutadiene rubber was incorporated into the matrix by the compositional quenching process. The average rubber particle size was a few micrometres or less. Primary amines were used to cure the epoxy resins. Methylene diisocyanate was selected to cross-link the phenoxy resins.

Tensile tests provide information about a material's response to a unidirectional load at a low strain rate. Molecules can adjust their conformation to the stress field and undergo plastic deformation when the load exceeds the yield strength of the material. Both pure epoxy and rubber-modified epoxy show little plastic deformation due to their tight network. Pure phenoxy shows some shear deformation. Yielding starts from internal flaws or surface defects and extends throughout the material. However, unstable crack growth results in a scatter in the data of the yield strain from 10–50%. Rubber inclusions in phenoxy resin provide

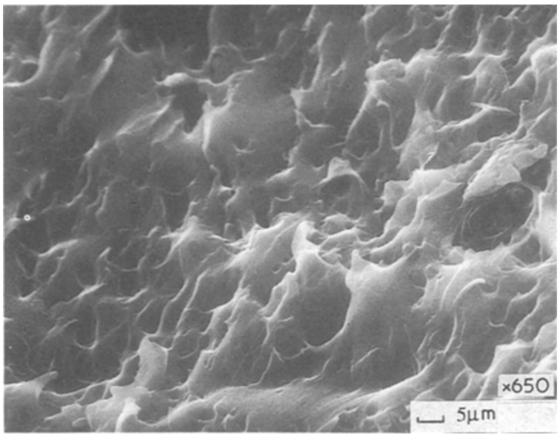


Figure 22 Fracture surface of uncrosslinked 20% rubber-modified phenoxy

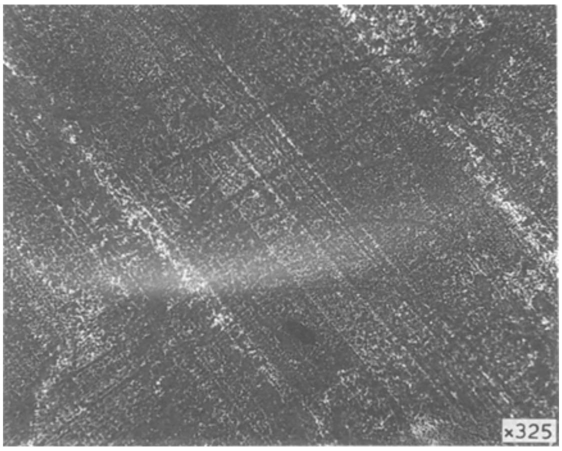


Figure 23 Transmission micrograph of MDI-cured phenoxy

multiple yielding sites on loading. If microshear bands form uniformly throughout the specimen, the matrix undergoes extensive plastic deformation and yield strains as high as 200% can be achieved.

An Izod impact test is perhaps the most severe test to examine the toughness of materials. A hammer is driven at a high strain rate into a notched sample. A systematic study of the effect of molecular mobility on impact toughness has been undertaken using MDI to cross-link phenoxy resins. At a fixed rubber content, the addition of MDI reduces the mobility of the phenoxy resin. The results indicate that only a few per cent of MDI is enough to restrict severely the plastic deformation with attendant losses in the impact toughness. Thus, the impact toughness decreases to the level of an epoxy system. This phenomenon has been observed in Nylon-6 systems which have been anionically polymerized with trifunctional activators [23]. A 50% reduction in Izod impact strength was observed when using 0.3 mol % triallyisocyanurate as the cross-linking agent. It also confirms that energy absorption by the rubber particles is negligible. If the molecules are flexible in response to impact, rubber inclusions provide multiple sites to initiate plastic deformation. Multiple microshear bands throughout the specimen account for the substantial increase in impact toughness.

The SEM observations provide a wealth of information and serve as a valuable complement to the mechanical characterization results. Photomicrographs of the fracture surface reveal rubber particle size and distribution details as well as details of the ability of the matrix to yield. The rubber particle size is approximately the same in both epoxy and phenoxy systems. However, the SEM fractographs show that the fracture surfaces of rubber-modified phenoxy are very rough. On the other hand, the fracture surfaces of both epoxy and cross-linked phenoxy show little matrix yielding. These SEM observations confirm the loss of impact strength in the thermoset system despite the addition of rubber.

The epoxy material has a very tight three-dimensional network and this results in a significant restriction in the amount of plastic deformation. For pure epoxies, the crack grows through the specimen by breaking chemical bonds. When the rubber-modified epoxies are subject to loads (tensile or impact), the rubber particles act as stress concentrators and initiate multiple microcracks around inclusions. Cracks nucleate and grow around the inclusions. Either micrometre or submicrometre size rubber particles are too large for the tight network structure. Thus, the change in crack growth path in the rubber-modified systems cannot compensate for the loss of the energy to break the chemical bonds of the pure epoxies.

Phenoxy resins provide a flexible matrix to study the rubber-toughening mechanisms. The addition of rubber into the phenoxy resin shows a profound effect on both the tensile and impact toughness. The rubber inclusions act as multiple shear yield-initiating sites, thus, permitting higher loads to be carried. Therefore, both ultimate tensile strength and impact strength are improved significantly. With the addition of cross-linking agents to the originally tough matrix, the molecules lose their mobility, and results similar to rubber-modified epoxies have been observed.

In conclusion, only bulk properties of rubber-modified plastics were investigated in this study. The rubber inclusion can be either a toughness modifier or a defect depending on the properties of the matrix. This study does not exclude the possibility of the application of rubber-modified thermosets in fibre-reinforced composites and as adhesives in which toughening mechanisms are different. When fracture occurs in the fibre-reinforced composites, debonding at the fibre/matrix interface and deformation in the matrix absorb the fracture energy and arrest crack propagation [24]. If the rubber-modified epoxies can promote the adhesion between the fibre and the matrix, the toughness of fibre-reinforced composites may be improved.

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