

# Effect of Elastomer Modification on the Adhesive Characteristics of Maleimide-Functional Phenolic Resins

C. GOURI, C. P. REGHUNADHAN NAIR, R. RAMASWAMY

Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram-695022, India

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**ABSTRACT:** The effect of addition of elastomeric modifiers on the adhesive properties like lap shear strength and T-peel strength of an addition curable, maleimide functional novolac phenolic resin (PMF), self-cured and cocured with a novolac epoxy resin, was studied using aluminium adherends. The modifiers used were (1) two grades of carboxyl terminated butadiene acrylonitrile copolymer (CTBN) of different molecular weights, (2) a low molecular weight, epoxidized hydroxyl-terminated polybutadiene, and (3) a high molecular weight acrylate terpolymer containing pendant epoxy functionality. The adhesive properties, when examined as a function of the varying concentrations of the additives, ranging from 10 to 30 parts per hundred parts (phr) of the resin, were found to depend on the nature of the matrix being modified as well as on the nature and concentration of the elastomer. The adhesive properties at ambient temperature of the self-cured, highly brittle PMF resin were dramatically improved by the inclusion of all the elastomers, the increase being substantial in the case of high molecular weight CTBN. For the more rigid, less ductile, epoxy-cured PMF system, the adhesive properties were marginally improved by the high molecular weight CTBN, whereas the other elastomers were practically ineffective. For both self-cured and epoxy-cured PMF systems, the inclusion of these elastomers generally decreased the high-temperature adhesive properties, implying impairment of thermal characteristics, evidenced also from their dynamic mechanical spectra. The presence of phase-separated elastomer particles in the modified systems has been evidenced from scanning electron micrographs. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2321–2332, 1999

**Key words:** maleimide-functional novolac; phenol-epoxy reaction; novolac epoxy; adhesives; elastomer-modified adhesives

## INTRODUCTION

The increasing applications of fiber-reinforced organic composites as structural components in weight-critical, high-technology areas like the aerospace and marine industries have placed greater demands on polymeric structural adhesive systems such as the epoxies and phenolics. Phenolics are versatile, low-cost polymers possessing several salient features required for a

high-temperature resistant polymer<sup>1,2</sup> and the characteristics that render them invaluable as adhesives are their capability to deliver water-, weather-, and high-temperature resistance to the bonded joints at relatively low cost.<sup>3</sup> Epoxies are extremely useful adhesives with good wetting abilities, mechanical properties, and chemical resistance.<sup>4</sup> When polymerized, these thermosetting resins provide amorphous, highly crosslinked networks that can result in many useful properties for engineering applications such as high modulus, low creep, and good performance at elevated temperatures. However, because of their high brittleness, the impact resistance and peel

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Correspondence to: C. P. R Nair.

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strength properties tend to be poor, invoking the need for alloying with other polymers to meet the requirements of specific applications. Commercially available, two-polymer alloy adhesives include vinyl-phenolics, nitrile-phenolics, nylon-epoxies, and elastomer-epoxies.<sup>5</sup>

The adhesive characteristics of an epoxy resin and its temperature profile can be tuned by the choice of the proper curative.<sup>6</sup> Phenolic resins, particularly novolac, serve as effective curatives for epoxy resins through the hydroxyl-epoxy reaction to provide amorphous, highly crosslinked networks possessing good mechanical strength and high temperature resistance<sup>7</sup>. However, the high brittleness and associated poor impact strength of phenolics and phenolic-epoxy systems render them *per se* unsuited for applications in structural adhesives. These problems are usually overcome through toughening the system with thermoplastics and/or elastomers.<sup>8,9</sup>

Recently, we reported a maleimide-functional novolac resin that cures principally through thermal polymerization of the imide group, exhibiting good adhesive characteristics and thermo-adhesive properties on self-curing and on curing through reaction with epoxy resins.<sup>10</sup> However, these systems were also found to suffer from the inherent brittleness characteristic of any phenolic system. Hence, it was of interest to study the adhesive characteristics of these systems on blending with selected elastomers so as to toughen them and thereby improve their adhesive properties.

This paper describes the effect of adding some selected elastomers on adhesive properties, notably the lap shear strength (LSS) and T-peel strength (TPS) of one such imido phenolic resin, both self-cured and cured through reaction with an epoxy resin. The effect of the nature and concentration of the additive on the adhesive properties and their high temperature retention have been investigated. The trend in properties has been correlated to their dynamic mechanical properties (DMA) and the resulting morphologies as observed by scanning electron microscopy (SEM).

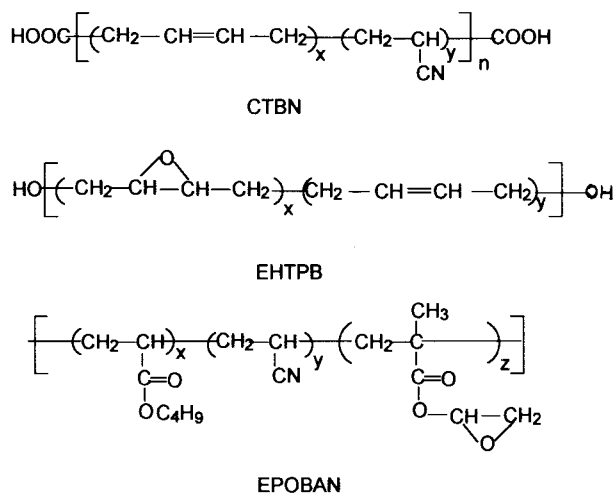
## EXPERIMENTAL

Phenol-maleimidophenol-formaldehyde copolymer (PMF) containing 28% by weight of maleimidophenol was synthesized as reported elsewhere.<sup>10</sup> PMF resin possessed a number average molecular

weight ( $M_n$ ) of 1110 g/mol with a dispersity of 5.3. This corresponds to a phenol functionality of 1.6 and imide functionality of 9.0. The novolac epoxy resin EPN 1139 (EPN), having functionality of 3.6 and epoxy value of 5.4 eq/kg, was procured from Hindustan Ciba Geigy (Mumbai, India) and was used as received. The elastomeric modifiers used were (1) carboxyl-terminated butadiene acrylonitrile copolymer (CTBN), (2) epoxidized hydroxyl-terminated polybutadiene (EHTPB), and (3) an epoxy functional butyl acrylate (BuA)-acrylonitrile (AN) copolymer (EPOBAN). Two different grades of CTBN were used. One was the solid-grade, high molecular weight polymer ( $M_n$  65000 g/mol), Nipol 1072 (hereafter referred to as CTBN-S), supplied by Zeon Chemicals, Inc., USA, having 0.07–0.08 ephr (eq/100 parts of resin) carboxyl content and 26–28% of AN. The other grade was the liquid, low molecular weight polymer ( $M_n$  3500 g/mol), Hycar 1300 × 8 (hereafter referred to as CTBN-L), supplied by B. F. Goodrich, USA, having 0.052 ephr carboxyl content and 18% of AN. EHTPB was an in-house product, prepared by the epoxidation of double bonds in HTPB (hydroxyl-terminated poly butadiene) using the performic acid method, as reported elsewhere.<sup>11</sup> EHTPB was a liquid resin with a molecular weight of  $M_n$  2200 g/mol and epoxy value 5.4 eq/kg. EPOBAN was another in-house product with a molecular weight of  $M_n$  55000 g/mol, dispersity 1.7, and epoxy value 0.2 eq/kg. It is essentially a copolymer of BuA and AN with 30–35% weight AN content. It has been covered in a recent patent application from this laboratory.<sup>12</sup> Commercial grades of triphenyl phosphine (TPP) and methyl ethyl ketone (MEK) were used as received. The structures of the elastomeric additives are shown in Scheme 1.

## Adhesive Preparation and Curing

CTBN-S was masticated in a two-roll mill and then dissolved in MEK to get approximately 20% solution. The exact dry residue was determined by evaporating a weighed quantity of the solution to constant weight in a hot air oven maintained at 100°C. Prereaction of either CTBN-S or CTBN-L with epoxy resin EPN was carried out at 80°C in nitrogen atmosphere, using 0.25 pbw (parts by weight) of TPP. For this, CTBN and EPN were taken on 1 : 1 weight basis (the solution in MEK was used in the case of CTBN-S) and the completion of the reaction was confirmed by monitoring the acid value. The exact dry residue of the pre-



**Scheme 1** Structures of elastomeric additives.

reacted solution of CTBN-S/EPN was determined as before. During the process of prereaction, the carboxyl groups of CTBN react with the epoxy groups to produce the epoxy-end-capped CTBN by the epoxy-carboxyl esterification reaction. This was further diluted with more of the epoxy to get the desired concentration levels of CTBN in the adhesive formulations.

Adhesive formulations of PMF resin or its blend with EPN (1 : 1 stoichiometry) with varying concentrations of the elastomeric modifiers were prepared as 50% solution in MEK and applied uniformly as a thin layer over the aluminium substrate. The solvent was allowed to evaporate by keeping the specimens in a hot air oven at 75–80°C for about 2 h. After cooling to ambient temperature, they were assembled together for testing adhesive properties. Curing was carried out in a hot air oven at 170°C for 30 min followed by 200°C for 30 min by applying a pressure of approximately 0.5 MPa over the bonded specimens using a lever press assembly. The optimization of the cure conditions has been detailed in a previous publication.<sup>10</sup>

### Testing of Adhesive Properties

LSS and TPS were determined using chromic acid etched B-51-SWP aluminium substrate as per American Society for Testing and Materials (ASTM) methods D-1002 and D-1876 respectively, using an Instron UTM Model 4202, at a cross-head speed of 10 mm/min. For determining LSS at 150°C, the specimens were soaked for a

period of 10 min at 150°C and then tested at that temperature.

### Preparation of Unidirectional (UD) Composites

The UD composites were made using E-glass fibers as reinforcement. The calculated number of tows of glass fiber were impregnated with a solution of the adhesives in MEK and dried at 50°C in vacuum. The strands were then compressed in a mold under a pressure of 2 MPa with a cure schedule of 30 min each at 170 and 200°C. The molded composite was cut into specimens of the required dimensions for DMA and interlaminar shear strength (ILSS) measurement.

### Evaluation of UD Composite

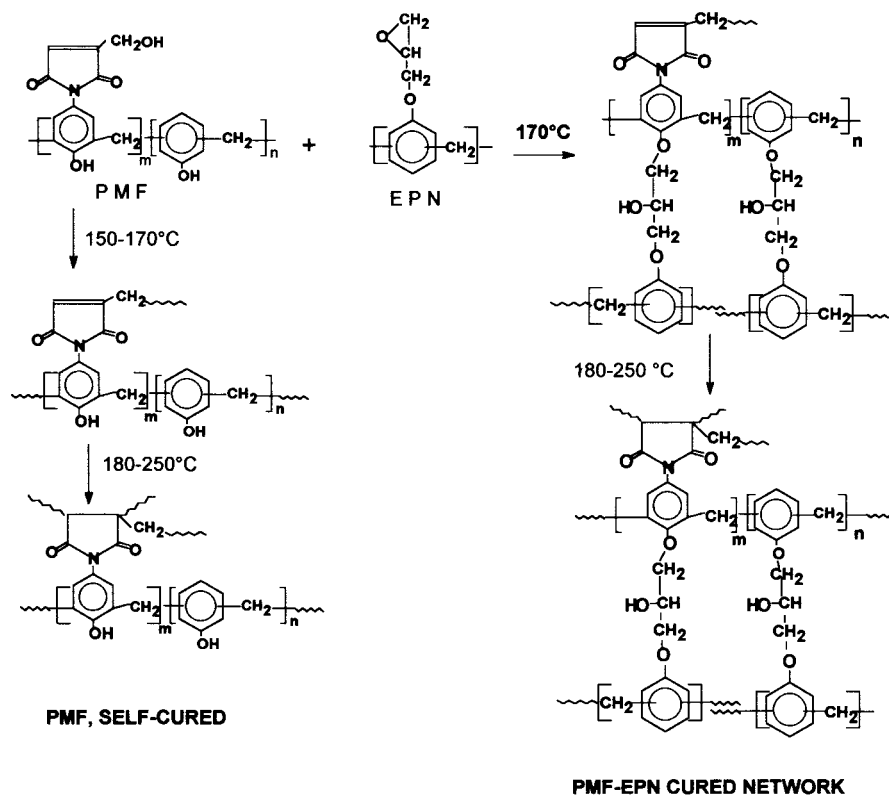
DMA of the composites was performed as per ASTM D-4092 in a DuPont Thermal Analyzer 2000, in conjunction with a DMA-983 at a frequency of 1 Hz, using specimens of dimension 60 × 6 × 1 mm. The ILSS of the composites was determined as per ASTM D-2344 in an Instron UTM model 4202 at a cross head speed of 1.3 mm/min using specimens of size 30 × 6 × 3 mm.

### SEM Analysis

The morphological features of the fractured surfaces of the samples coated with gold using a vacuum sputterer were observed using a Stereoscan 250 MK-3 Cambridge instrument at an accelerating voltage ranging from 9.6 to 21 KV; the individual values have been shown in the electron micrographs.

## RESULTS AND DISCUSSION

The PMF copolymer is a new class of phenolic resin possessing maleimide functions and capable of undergoing addition cure through polymerization of the maleimide groups. The structure and mechanisms of cure are shown in Scheme 2. The resin possesses a small amount (3–5% by weight) of methylol groups on the maleimide ring capable of conferring partial condensation character to it. In a previous study, it was found that the PMF resin acts as a poor adhesive when self-cured and as a good adhesive on cocuring with epoxy resin.<sup>10</sup> Epoxy-cured PMF resin was found to provide better adhesive characteristics and superior thermo-adhesive profile when compared to similarly



**Scheme 2** Mechanisms of cure reactions of PMF resin.

cured conventional novolac resin. However, the system was found to undergo brittle fracture. For moderately good load-bearing applications, it is necessary to render it tougher.

The conventional way of toughening a brittle matrix is by way of blending it with thermoplastics or elastomers.<sup>8,9</sup> The bulk of the research on the toughening of thermosets has been focused on epoxies, especially the diglycidyl ether of bisphenol A (DGEBA) resin systems. CTBN has been the most widely studied epoxy toughening agent,<sup>8,9,13,14</sup> the others including ATBN (amine-terminated butadiene acrylonitrile copolymer),<sup>15</sup> CTPPGA [carboxyl-terminated poly(propylene glycol adipate)],<sup>16</sup> CTPEGA [carboxyl-terminated poly(ethylene glycol adipate)],<sup>17</sup> thermoplastics<sup>18</sup> like poly(aryl ether ketones), polysulfones, acrylic elastomers,<sup>19-21</sup> and preformed core-shell polymers. In this work, PMF and PMF/EPN resins were blended with three elastomers, CTBN, EHTPB, and EPOBAN. The adhesive properties of PMF resin alone and cocured with EPN and modified with the above elastomers are presented here.

## Modification Using CTBN-S and CTBN-L

### Self-Cured PMF

The adhesive properties of self-cured and epoxy-cured PMF (PMF/EPN) resin, when modified with the two grades of CTBN, are given in Tables I and II. The absolute LSS and TPS values of self-cured PMF resin are poor because the system on curing through the maleimide provides a very brittle matrix. Addition of both CTBN-S and CTBN-L brings about a dramatic improvement in LSS. The relative improvement in LSS brought about by these additives has been depicted in Figure 1. The increase is more pronounced in the case of CTBN-S. It can be observed that at about 30 phr loading of CTBN-S, the LSS value is enhanced to a 700%, whereas for the optimum loading of 15 phr of CTBN-L, the increase is only to 250%. The TPS was also substantially improved by the inclusion of CTBN-S and it can be seen to increase almost linearly with the rubber content. On the other hand, the low molecular weight version was absolutely ineffective for the peel property.

**Table I Effect of CTBN-S on the Adhesive Properties of PMF and PMF/EPN Systems**

Conc. of the Additive (phr)	Self-Cured PMF			PMF/EPN		
	LSS (MPa)		TPS at RT (kN/m)	LSS (MPa)		TPS at RT (kN/m)
	RT <sup>a</sup>	150°C		RT	150°C	
0	2.1	3.5	0.01	17.0	14.3	0.56
10	5.3	5.2	0.43	18.5	10.6	1.20
15	8.0	4.5	0.64	20.0	9.4	1.70
20	11.3	4.3	0.70	20.0	7.8	2.00
30	14.3	3.9	1.00	20.0	6.5	2.00

<sup>a</sup> RT: room temperature.

The enhancement in adhesive properties in this case can be attributed to the reduction in the brittleness of the cured network brought about by the incorporation of long-chain, aliphatic CTBN. Minor reactive blending of PMF with CTBN could occur during the curing process through reaction of their hydroxyl and carboxyl groups, respectively. The toughness improvement of the matrix is brought about by the two-phase morphology formed during the curing process by the controlled precipitation of rubbery particles from the initially compatible thermoset-elastomer mixture as is generally the toughening mechanism of CTBN in brittle matrices.<sup>22</sup> SEM Figures 2(a) and 2(b) show the morphologies of self-cured PMF, unmodified and modified with 10 phr of CTBN-S, respectively. PMF on curing gives off low molecular weight condensation products, thus showing a foaming nature, which is visible in Figure 2(a), whereas the dispersed elastomer phase is evident in Figure 2(b). The precipitated rubber can arrest crack propagation to a greater extent during fracture by distributing the applied stress over the whole bond area. Similar toughening mechanisms

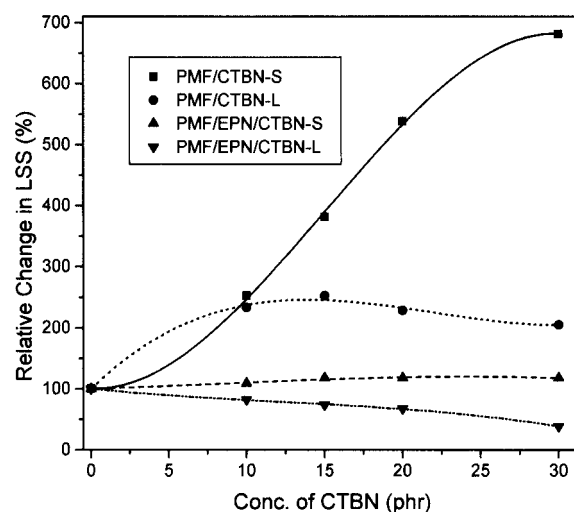
have been found operative in many brittle matrices.<sup>22</sup> Compared to CTBN-S, the lower performance of CTBN-L could be due to the better dispersion of the low molecular weight grade in the matrix producing a pseudo homogenous mixture, as a result of which the plasticization effect outweighs the toughening effect.

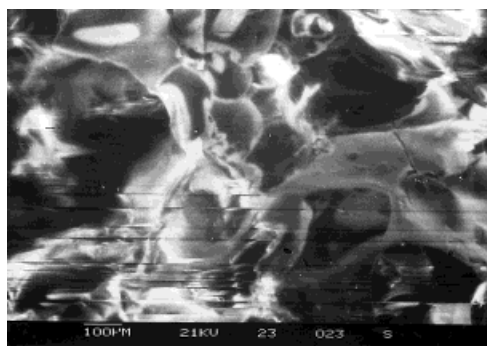
#### PMF/EPN System

When cocured with epoxy resin, the adhesive properties of PMF improved significantly due to the introduction of polar epoxy groups into the matrix that possess better wetting properties and yield better adhesion to metallic substrates. Moreover, the cohesive strength of the adhesive is improved by means of the increased crosslinking

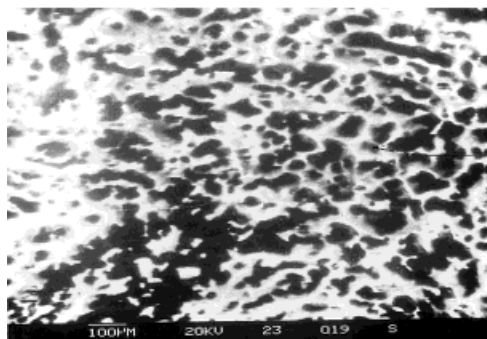
**Table II Effect of CTBN-L on the LSS (in MPa) of PMF and PMF/EPN Systems**

Conc. of the Additive (phr)	Self-Cured PMF		PMF/EPN	
	RT	150°C	RT	150°C
	0	2.1	3.5	17.0
10	4.9	4.2	14.0	3.6
15	5.3	3.5	12.5	3.3
20	4.8	3.3	11.5	3.0
30	4.3	2.5	6.5	2.0

**Figure 1** Variarion of relative increase in LSS of PMF and PMF/EPN systems with concentration of CTBN-S and CTBN-L.



(a)



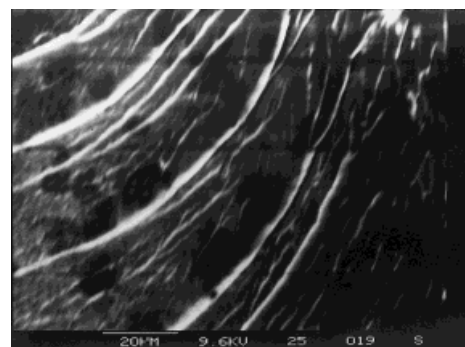
(b)

**Figure 2** SEM of self-cured PMF (a) unmodified (b) modified with 10 phr of CTBN-S.

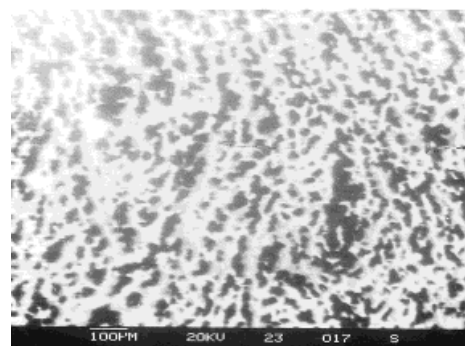
imparted by the inclusion of polar hydroxy-ether groups into the cured system. The optimum formulation for epoxy cocured system (PMF/EPN) had been obtained based on 1 : 1 phenol-epoxy stoichiometry.<sup>10</sup> With the inclusion of CTBN-S, the adhesive properties improved further, but only marginally. Cocuring with epoxy had increased the crosslink density of the system, thereby making it more rigid and less amenable to toughening with elastomers. It is acknowledged that elastomers cannot toughen highly crosslinked, rigid matrices.<sup>23,24</sup> Hence, the effectiveness of CTBN in improving the adhesive properties of PMF/EPN is not as much as in the case of self-cured PMF, which although brittle, is less rigid and crosslinked. The relative effectiveness of CTBN-S and CTBN-L in modifying the adhesive properties of PMF/EPN system has also been demonstrated in Figure 1. Whereas CTBN-S was moderately effective in improving the LSS, the low molecular weight CTBN-L was found to adversely affect the adhesive properties of this system, in all proportions.

The morphologies of the PMF/EPN system, unmodified and modified with CTBN-S and CTBN-

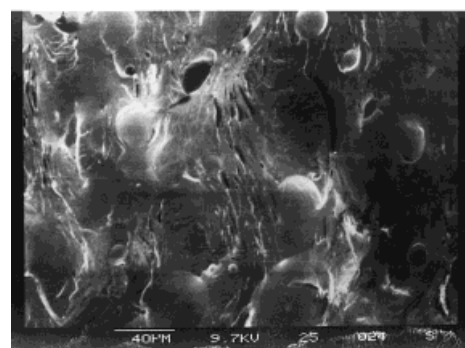
L, are presented in Figures 3(a–c), respectively. Compared to self-curing, cocuring with epoxy has rendered the matrix more rigid and has reduced the foaming nature significantly. SEM of the unmodified system reveals the complete miscibility of phenolic and epoxy resins and the morphology obtained is characteristic of brittle fracture with cracks in different planes [Fig. 3(a)]. With the incorporation of CTBN-S (10 phr), a two-phase morphology is obtained with a uniformly dis-



(a)



(b)



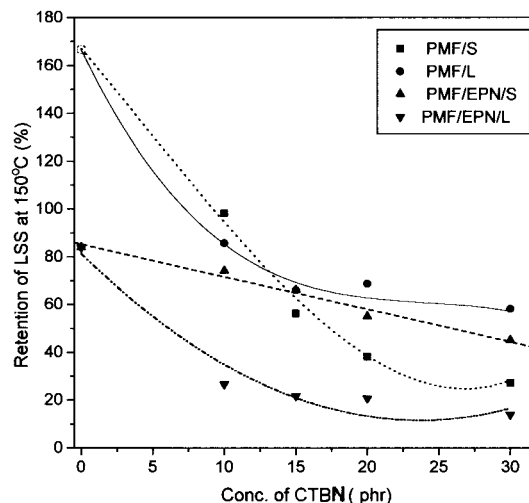
(c)

**Figure 3** SEM of PMF/EPN (a) unmodified (b) modified with 10 phr of CTBN-S, and (c) modified with 20 phr of CTBN-L.

persed elastomer phase [Fig. 3(b)]. However, in the epoxy cocured system, being highly rigid, this phase-separated morphology was found to further enhance the adhesive properties only marginally. In the case of CTBN-L (20 phr), a nonuniform distribution of globular particles was observed, ranging in size from 20 to 70 microns [Figure 3(c)]. The decreased polarity of CTBN-L compared to CTBN-S, leads to lesser compatibilization with PMF/EPN, thereby producing a coarser dispersion of the elastomer. This morphology also did not improve the adhesive properties of the system. Such larger particles fail catastrophically during fracture and, hence, cause a diminution of adhesive properties.

In the modification of the highly crosslinked epoxy matrix, reactive rubbers such as CTBN have been reported as ineffective modifiers.<sup>23–26</sup> It has also been observed that ductility of the matrix is necessary to some extent to decrease the brittleness of the resin, to be effectively modified by the reactive elastomers.<sup>27,28</sup> In the present study we also find that the reactive elastomer CTBN, which could substantially enhance the adhesive properties of the brittle, less crosslinked PMF system, could not be effective in the case of the more rigid, epoxy-cocured matrix.

The two additives varied in a similar pattern in their capability for retaining the LSS of the modified matrices at higher temperatures. The LSS properties at 150°C for the systems are presented in Tables I and II. The comparative LSS retention of the different systems and their dependency on elastomer concentration can be found in Figure 4. It was observed that LSS at 150°C as well as the % retention of LSS at this temperature were adversely affected by the inclusion of both grades of CTBN. This is attributed to thermally induced softening of the rubbery phase that promote debonding. Compared to rubber-modified PMF/EPN, rubber-modified PMF system is more prone for changes in viscoelastic character with temperature, due to its higher brittleness. This leads to a more drastic fall in retention of the property at 150°C with increase in elastomer concentration, for the self-cured PMF system. For PMF/EPN system, the decrease is less catastrophic with the high molecular weight rubber. The lower retention in the case of CTBN-L is ascribable to its increased molecular mobility at this temperature, facilitating debonding more than in the case of the high molecular weight analogue.



**Figure 4** Variation in Retention of LSS at 150°C of the PMF and PMF/EPN systems, with concentration of CTBN-S and CTBN-L.

#### Modification Using EHTPB and EPOBAN

Both EHTPB and EPOBAN contain epoxy functions along the chain. Whereas in the former it is internal epoxy, the latter contains epoxy groups in pendant positions. EHTPB has been shown to impart toughness to DGEBA epoxy systems with a resultant enhancement in adhesive properties.<sup>11</sup> EPOBAN, containing polar nitrile groups, has been shown to be a good adhesive by itself.<sup>12</sup> Reactive acrylic elastomers based on BuA/AN/glycidyl methacrylate have been used as epoxy modifiers by T. Ijima et al.<sup>19–21</sup> Both EHTPB and EPOBAN could be served as a matrix modifier as well as curative for the PMF resin. The effects of variation of EHTPB and EPOBAN concentration in the PMF and PMF/EPN systems, for their LSS properties at ambient temperature and at 150°C, are given in Table III. For self-cured PMF, LSS at ambient temperature is found to increase by the addition of both elastomers, although the enhancement is less pronounced than in the case of CTBN. The improvement is principally caused by the cure reaction of the epoxy groups with the phenol groups. The reaction could lead to a good dispersion of both the elastomers in the matrix, thereby reducing its brittleness. EHTPB is found to be better in enhancing the adhesive strength, as shown in Figure 5. This must be due to its higher epoxy content leading to establishment of larger number of bonds per unit volume (increased crosslink density). But for the difference in crosslink density, EPOBAN would be expected

**Table III** LSS (in MPa) of PMF and PMF/EPN System Modified by EHTPB and EPOBAN

Conc. of the Additive (phr)	EHTPB				EPOBAN			
	Self-Cured PMF		PMF/EPN		Self-Cured PMF		PMF/EPN	
	RT	150°C	RT	150°C	RT	150°C	RT	150°C
0	2.1	3.5	17.0	14.3	2.1	3.5	17.0	14.3
10	3.5	2.2	16.0	6.3	2.2	2.6	15.4	4.9
15	4.6	1.8	14.7	5.3	—	—	—	—
20	5.4	1.7	13.2	3.6	3.3	2.4	16.6	5.3
30	5.8	0.8	12.9	2.5	—	—	—	—

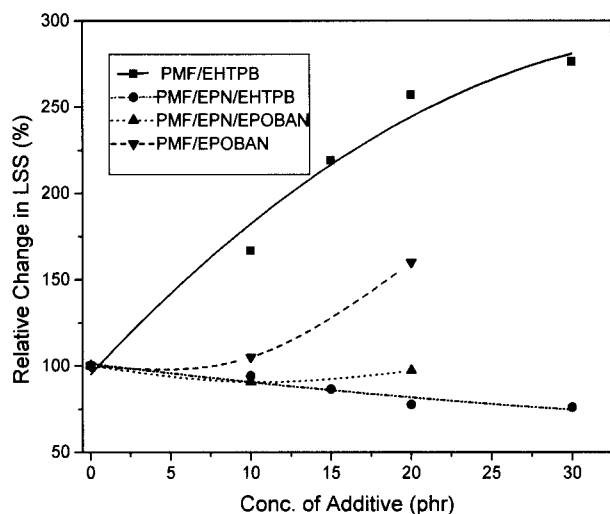
to furnish better improvement in analogy to CTBN due to the presence of polar, high cohesive acrylonitrile groups in it.

It is observed that for the PMF/EPN system, like CTBN-L, these elastomers also lead to a gradual decrease in the adhesive characteristics, the relative variation being shown in Figure 5. As stated earlier, the PMF/EPN system being highly rigid and crosslinked, the addition of the elastomer does not contribute to the toughness. It appears that the elastomers compete with EPN for reaction with the phenol, partly impeding the phenol-EPN reaction. This is particularly so in the case of EHTPB. For example, the incorporation of 20 phr of EHTPB alters the phenol-epoxy stoichiometry by an extent of 0.33 equivalents. This results in an overall decrease in crosslink

density and the plasticization caused by the elastomers contribute to the slight diminution in properties. On a comparative scale, EPOBAN participates in the crosslinking reaction to a lesser extent than EHTPB since the former contains less epoxy functions. From Figure 5, it can be seen that the decrease in LSS at 150°C is less significant for EPOBAN, where the cohesive force imparted by the nitrile group compensates, to some extent, the reduction in crosslink density.

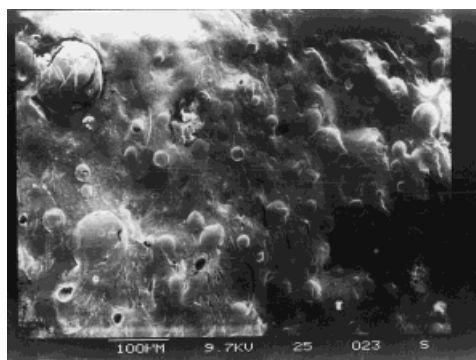
The morphologies of the PMF/EPN system modified with 20 phr of EHTPB and EPOBAN respectively are shown in Figures 6(a) and 6(b). An elastomer-precipitated morphology is obtained for both cases, with a nonuniform distribution. The particles vary in size from 20 to 70 microns for EHTPB- and 50 to 200 microns for EPOBAN-modified systems. EHTPB, having the butadiene backbone, is less polar compared to the phenolic-epoxy matrix and this might be leading to the phase separation of larger particles. Still larger particles, seen in the case of EPOBAN system, could be due to the much reduced interaction of EPOBAN with the matrix compared to EHTPB because of the former's very low functionality. As observed in the case of CTBN-L, these bigger particles are inefficient in arresting the crack propagation during fracture and, hence, are not capable of improving the toughness of the systems.

The retention of LSS at 150°C, compared to the respective values at ambient temperature for PMF and PMF/EPN systems in the presence of these two elastomers, is demonstrated in Figure 7. All systems show tremendous decrease in the values. The fall is sharper for the PMF system than the PMF/EPN one. Since the absolute values of the room temperature LSS of the PMF system

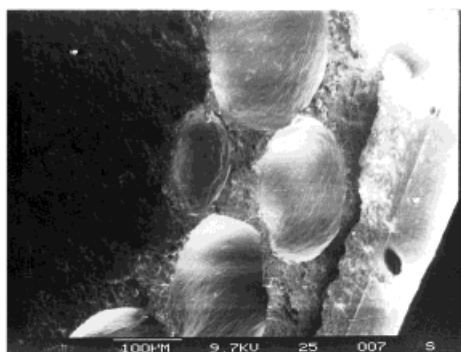


**Figure 5** Variation of relative increase in LSS of the PMF and PMF/EPN systems with concentration of EHTPB and EPOBAN.





(a)



(b)

**Figure 6** SEM of PMF/EPN modified with (a) 20 phr of EHTPB and (b) 20 phr of EPOBAN.

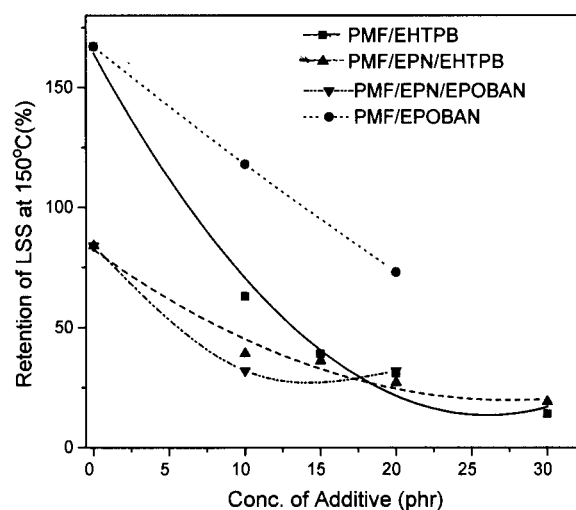
increase with increase in elastomer content, the decrease in absolute LSS value with rise in temperature and increase in elastomer content is tremendous, as can be noted from the values compiled in Table III. The comparatively better LSS retention at 150°C of EPOBAN system is due to the better thermal stability of the acrylonitrile-containing polymer. It has been observed that EPOBAN undergoes additional crosslinking at around 200°C, due to the addition reaction of nitrile groups. This may also be contributing to its enhanced retention of adhesive properties at high temperatures. The relative decrease in high-temperature LSS with composition is less pronounced for the EPN-cured system. Here again, the EPOBAN-modified system tends to show marginal superiority when present in higher concentrations (Fig. 7).

In one experiment, EHTPB was used in differing proportions with EPN resin for curing PMF resin, so that the total stoichiometry of 1 : 1 for hydroxyl/epoxy was maintained. LSS at ambient as well as at 150°C obtained with these systems

are presented in Table IV. LSS at ambient temperature was found to be less sensitive to the epoxy combinations. However, the LSS at higher temperature was highly dependent on the presence of EHTPB. When EPN is replaced, even to a small extent, with the elastomeric EHTPB as curative, the high-temperature LSS properties were found to be catastrophically reduced, due to the dispersion of the latter and its high temperature flexibility.

### DMA Analysis

With a view to correlating the observed adhesive performance to the dynamic mechanical properties, DMA of the cured adhesives were analyzed. Since the resins could not be easily molded to the DMA specimen requirements, they were examined as their UD composites with glass fiber of the same resin content (40% by volume) for all systems. The DMA traces are shown in Figure 8. The absolute value of dynamic storage modulus ( $E'$ ) at a given temperature is indicative of the stiffness of the resin since the contribution of the reinforcement is the same in all cases. All modified systems contain 20 phr of the elastomer. Generally, it is found that the  $E'$  decreases with the additive. The decrease is less pronounced for EHTPB and CTBN-L, which possess appreciable functional groups for coreaction with the matrix. In terms of the coreaction of part of EHTPB and CTBN-L: although it reduces the crosslink density of the



**Figure 7** Variation in retention of LSS at 150°C of the PMF and PMF/EPN systems with concentration of EHTPB and EPOBAN.

**Table IV** Effect of Variation of EPN/EHTPB Ratio on LSS of PMF/EPN/EHTPB System with 1 : 1 Effective Phenol/Epoxy Equivalent Ratio

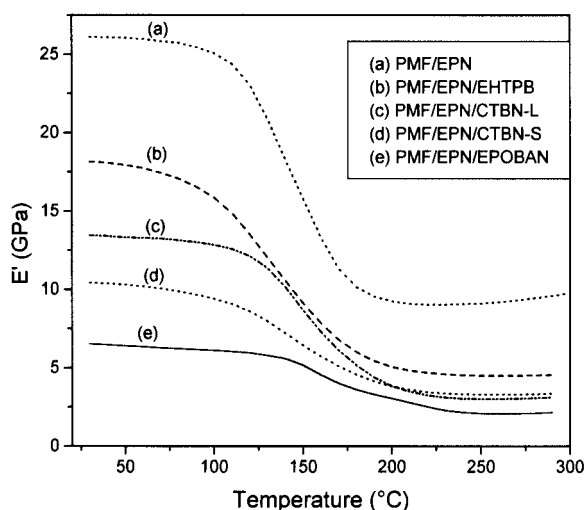
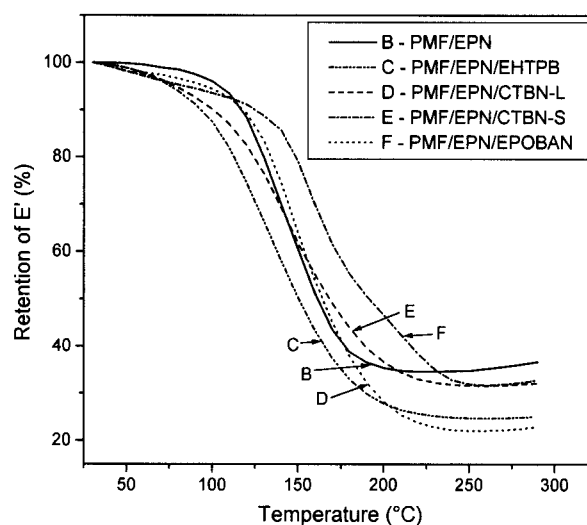
Equivalent Ratio of EPN : EHTPB	Weight % of EHTPB	LSS at RT (MPa)	LSS at 150°C (MPa)	% Retention of LSS at 150°C
1 : 0	0	17.0	14.3	84
2 : 1	20	18.0	3.4	19
1 : 1	30	17.0	2.0	12
1 : 2	40	16.3	1.3	8
0 : 1	60	16.0	1.0	6

matrix, this reduction is much less than in the case of CTBN-S and EPOBAN, which are high molecular weight polymers.

For a true comparison of the composition dependency on the glass transition ( $T_g$ ), the retention of  $E'$  with temperature for different systems is shown in Figure 9. The  $\tan \delta$  peak temperatures of the systems along with their % retention of  $E'$  and LSS at 150°C are given in Table V. The transition is represented by the PMF phase, since the elastomer phase might be showing its characteristic  $T_g$  below room temperature (not shown in this figure). Both CTBN-S and CTBN-L do not affect the  $T_g$  or % retention of  $E'$  at 150°C. This means that their phases make clean boundaries and are not embedded in the PMF/EPN matrix, despite the possible coreaction. EHTPB is dissolved and probably partly coreacted in the matrix, with the result that its  $T_g$  is brought down. EPOBAN is not likely to coreact significantly but

its better dissolution and partial crosslinking through the addition reaction of the nitrile group enhances the  $T_g$  marginally. This has also been reflected in the better retention of  $E'$  as well as LSS at 150°C of the EPOBAN-containing system compared to EHTPB system (Fig. 7 and Table V). Since the thermo-adhesive profile of the CTBN systems does not bear any correlation to the temperature dependency of the DMA behavior of these systems, it may be concluded that in these cases, fracture is mostly at the interphase. DMA profiles may indicate the adhesive behavior only in the case of cohesive failure. As is evident from Table V, no direct correlation was observable between the retention of mechanical properties ( $E'$ ) and that of the adhesive properties (LSS) at 150°C.

The ILSS is a measure of the resin-reinforcement interaction and can, *a priori*, indicate the

**Figure 8** DMA traces of neat and elastomer-modified PMF/EPN systems.**Figure 9** Variation in retention of  $E'$  with temperature for neat and elastomer-modified PMF/EPN systems.

**Table V Characteristics of UD Composites and % Retention of LSS at 150°C of Elastomer-Modified PMF/EPN Systems**

Additive	Conc. of Additive (phr)	tan $\delta$ Peak (°C)	Retention of $E'$ at 150°C (%)	Retention of LSS at 150°C (%)	ILSS (MPa)
NIL	NIL	160	60.4	84	85.5
CTBN-S	20	162	61.7	55	38.3
CTBN-L	20	172	65.1	21	20.3
EHTPB	20	158	50.2	27	44.0
EPOBAN	20	161, 218 <sup>a</sup>	79.0	32	37.7

<sup>a</sup> Second tan  $\delta$  due to self-polymerization of the nitrile functions.

adhesive characteristics of the resin if the fracture of the composite is at the interphase. The ILSS properties of all elastomer-modified systems (Table V) were found to be less than the unmodified system. In general, the decrease could be attributed to the reduced crosslink density and decreased wetting properties of the modified systems. The elastomers adversely affect the bonding of the matrix resin on to the glass fibers and weaken the interphase. The same mechanism may also be operative in the case of aluminium adherend. Among the modified systems, the better strength was obtained for the EHTPB system, probably due to its higher crosslink density by virtue of its higher epoxy content.

## CONCLUSIONS

The adhesive properties of PMF resin self-cured and cocured with epoxy systems when modified with the addition of elastomers like CTBN, EHTPB, and EPOBAN were found to depend on the nature and concentration of the elastomer as well as on the nature of the thermoset matrix being modified. All the elastomers were effective in increasing the adhesive properties at ambient temperature of the brittle, less crosslinked self-cured PMF. CTBN-S was the most effective additive with a good phase-separated morphology. For the epoxy cocured phenolic system, which is more rigid and cross-linked compared to the self-cured one, except for a marginal increase by CTBN-S, all the other elastomers were ineffective in improving the adhesive properties. The requirement that the matrix should have a minimum ductility to be effectively toughened by the elastomer was also substantiated in this study. The inclusion of these elastomers generally decreased the high-

temperature adhesive properties. For a given composition, the decrease was sharper for CTBN-L than CTBN-S, due to the reduced compatibility of the former in the matrix. Similarly, between EPOBAN and EHTPB the former was comparatively better in retaining the LSS at high temperature, due to its crosslinking through the addition reaction of the nitrile groups.

A DMA study of the elastomer-modified PMF/EPN system has shown that the absolute values of  $E'$  are reduced with the inclusion of these elastomers, whereas the tan  $\delta$  temperatures remain almost unaffected. SEM analysis shows the single phase morphology for the unmodified PMF and PMF/EPN systems and phase-separated morphology for the elastomer-modified ones. The size and state of the precipitated secondary phase depend on the molecular weight as well as the chemical reactivity of the added elastomer. For the CTBN-S-modified systems, the dispersed phase was rather continuous and this morphology led to the maximum improvement in adhesive properties. For the CTBN-L-, EHTPB-, and EPOBAN-modified PMF/EPN systems, the dispersed phase was nonuniform with a wide distribution of particle sizes. These particles were rather too large to be effective in improving the toughness of the system and hence reduced the adhesive properties.

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## REFERENCES

- Knop, A.; Pilato, L. A. *Phenolic Resins: Chemistry, Applications and Performance, Future Directions*; Springer-Verlag: Heidelberg, 1985; p 31.

2. Reghunadhan Nair, C. P.; Bindu, R. L.; Ninan, K. N. In *Metals, Materials and Processes*; Radhakrishnan, G., Ed.; Meshap Publications: Mumbai, India, 1997; Vol 9(2), p 179–200.
3. Pizzi, A. In *Handbook of Adhesive Technology*; Pizzi, A., Mittal, K. L., Eds.; Marcel Dekker: New York, 1994; p 329.
4. Garnish, E. W. In *Structural Adhesives: Developments in Resins and Primers*; Kinloch, A. J., Ed.; Elsevier Applied Science Publishers: London, 1986; p 57–76.
5. Rayner, C. A. A. In *Adhesion and Adhesives*; Houwink, R., Salomon, G., Eds.; Elsevier Publishing Company, New York, 1968; Vol 1, p 318–337.
6. Wright, C. D.; Muggee, J. M. In *Structural Adhesives: Chemistry and Technology*; Hartshorn, S. R., Ed.; Plenum Press: New York, 1986; 113–166.
7. Mika, T. F.; Bauer, R. S. In *Epoxy Resins: Chemistry and Technology*; May, C. A., Ed.; Marcel Dekker: New York, 1988; p 481.
8. Kinloch, A. J. In *Structural Adhesives: Developments in Resins and Primers*; Kinloch, A. J., Ed.; Elsevier Applied Science Publishers: London, 1986; 127–162.
9. McGarry, F. J. In *Polymer Toughening*; Arends, C. B.; Ed.; Marcel Dekker: New York, 1996; p 175–186.
10. Gouri, C.; Reghunadhan Nair, C. P.; Ramaswamy, R. *J Appl Polym Sci* 1999, 73, 695–705.
11. Latha, P. B.; Adhinarayanan, K.; Ramaswamy, R. *Int J Adhesion Adhesives*, 1994, 14(1), 57–61.
12. Reghunadhan Nair, C. P.; Sivadasan, P. *Indian Patent Appln.* 451/MAS/99 (21-4-99).
13. Dusek, K.; Lednický, F.; Lunak, S.; Mach, M.; Duskova, D. In *Rubber-Modified Thermoset Resins*; Riew, C. K., Gillham, J. K., Eds.; *Advances in Chemistry Series 208*; American Chemical Society: Washington DC, 1984; p 27–35.
14. Ting, R.Y. In *Epoxy Resins Chemistry and Technology*, 2nd ed.; May, C. A., Ed., Marcel Dekker: New York, 1988; p 551–601.
15. Levita, G.; Marchetti, A.; Butta, E. *Polymer* 1985, 26, 1110–1116.
16. Sasidharan Achary, P.; Gouri, C.; Ramaswamy, R. *J Appl Polym Sci* 1991, 42, 743–752.
17. Ratna, D.; Chakraborty, B. C.; Deb, P. C. *J Polym Mater* 1997, 14, 189–194.
18. Bauer, R. S.; Stenzenberger, H. D.; Romer, W. 34th *Int SAMPE Symp* 1989, 8, 312.
19. Ijima, T.; Tomoi, M.; Yamasaki, J.; Kakiuchi, H. *Eur Polym J* 1991, 27, 851.
20. Ijima, T.; Horiba, T.; Tomoi, M. *Eur Polym J* 1991, 27, 1231.
21. Ijima, T.; Yoshioka, N.; Tomoi, M. *Eur Polym J* 1992, 28(6), 573–581.
22. Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. *Polymer* 1983, 24, 1346–1353.
23. Bucknall, C. B.; Partridge, I. K. *Polymer* 1983, 24, 639.
24. Diamond; Moulton, R. J. 29th *Nat SAMPE Conf* 1984, 422.
25. Yee, A. F.; Pearson, R. A. *J Mater Sci* 1986, 21, 2462–2475.
26. Pearson, R. A.; Yee, A. F. *J Mater Sci* 1989, 24, 2571.
27. Manzione, L. T.; Gillham, J. K.; McPherson, C. A. *J Appl Polym Sci* 1981, 26, 907.
28. Kirschenbaum, S. L.; Bell, J. P. *J Appl Polym Sci* 1985, 30, 1875.