Adhesive and Thermal Characteristics of Maleimide-Functional Novolac Resins

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ABSTRACT: A novel, addition-curable maleimide-functional novolac phenolic resin was evaluated for adhesive properties such as lap shear strength and *T*-peel strength using aluminium adherends, when thermally self-cured and cocured with epoxy resins. The adhesive properties of the self-cured resin, although inferior at ambient temperature, improved at high temperature and were found to depend on the cure conditions. When cocured with epoxy resin, the adhesive properties improved significantly and showed a strong dependence on the nature of the epoxy resin used, on the stoichiometry of the reactants, on the concentration of imide groups in the phenolic resin, and on the extent of polymerization of the maleimide groups. Optimum adhesive properties were obtained for novolac resins with a moderate concentration of maleimide groups, taken on a 1:1 hydroxyl–epoxy stoichiometry with a novolac epoxy resin. In comparison to the conventional novolac, the imide–novolac contributed to improved adhesion and better adhesive property retention at higher temperature when cured with the novolac–epoxy resin. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 695–705, 1999

Key words: maleimide-functional novolac; phenol-epoxy reaction; novolac epoxy; adhesives, *N*-(4-hydroxy)phenylmaleimide; addition-cure phenolics

INTRODUCTION

The demand for high-performance and high-temperature resistant structural adhesives is on the increase, in view of the rapid expansion in high-tech areas like the aerospace industry.¹ High-temperature adhesives are required in many different applications in advanced aircrafts, space vehicles, missiles, ground vehicles, and electronics. Their use involves the joining of metals, composites, ceramics, films, and their combinations. Although each application may have a unique set of requirements, the common criterion is high-temperature stability, that is, the adhesive must withstand the processing temperature and must be able to perform at the use temperature for the required service period. A large

variety of heterocyclic aromatic polymers such as polyimide, polybenzimidazole, polyquinoxaline, and polypyrrone have been identified as high-temperature adhesives.²⁻⁴ Although many of these polymers show promise as high-temperature adhesives, their syntheses and applications require stringent conditions. Ideally, for application as an adhesive, the polymer should be processible under moderate conditions with no volatile evolution and should be thermally stable. Further, it should be compatible with the adherends and should have good, durable properties. Only a few high-temperature polymeric adhesives are commercially available because of an elusive market and an unfavorable combination of price, processibility, and performance. Such polymers are often made and used for specialized applications and are generally not available commercially.

Phenolic resins are versatile polymers, possessing several salient features required of a

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high-temperature-resistant polymer.^{5,6} The characteristics that render the phenolic resins invaluable as adhesives are their capability to deliver water, weather, and high-temperature resistance to the bonded joints at a relatively low cost.⁷ However, their unrestricted entry into the area of structural adhesives has been hampered mainly by the inherent brittleness and also because of the evolution of volatiles during their cure. A tough phenolic adhesive formulation necessitates blending with rubber, which could result in a drastic reduction in the properties at high temperatures.⁸ Conventional phenolic resins cure at high temperature by a condensation mechanism with the evolution of volatiles and this necessitates the application of high pressure during the adhesive bonding to get void-free glue lines. Moreover, the need for the use of a catalyst for curing (of novolacs) and the limited shelf-life of the resins (e.g., resole) at ambient temperature are also major shortcomings of phenolics.

With a view to overcome these shortcomings of phenolic resins, much research is being carried out in developing addition-cure phenolics. Such novolac resins bearing addition-cure groups such as allyl,⁹ vinyl,⁶ propargyl,⁶ bisoxazoline,¹⁰ benzoxazine,¹¹ and maleimide^{12,13} are made to undergo curing through the polymerization of these groups to furnish a thermally stable network. Such addition-cure phenolics appear to be better suited than are resoles for adhesive formulations, since no volatiles emanate in the former. Recently, our laboratory developed an addition-curable novolac resin that cures through the polymerization of maleimide functions.^{12–14} It was of interest to evaluate the adhesive characteristics of this system bearing the polar imide group. This article describes studies on the adhesive characteristics of this maleimide-functional novolac, alone and in combination with epoxy curatives. A part of this study was presented earlier.¹⁵ The adhesive properties and their temperature dependencies were correlated with the possible network structure in comparison with a conventional novolac. The study also encompasses cure optimization and the thermal properties of the cured network in relevant cases.

EXPERIMENTAL

Materials

The epoxy resins were of commercial grade procured from Hindustan Ciba Geigy (Mumbai, India) and were used as received. GY-250 and CT-200 are diglycidyl ether of bisphenol A (DGEBA) resins with epoxy values of 5.5 and 2.1 equivalents/kg, respectively. EPN-1139 (EPN) is a novolac epoxy resin having an epoxy value of 5.5 equivalents/kg and a functionality of 3.6. Laboratory-grade methyl ethyl ketone (MEK) was used as received. Silane-treated E-glass fiber (Unnathi Corp., Ahmedabad, India) with a thickness of 7 mil and a density of 2.4 g/cc was used as received. N-(4-hydroxy)phenylmaleimide (HPM) was synthesized by a reported procedure.¹⁶

Synthesis of Phenol-(4-hydroxy)phenylmaleimide-Formaldehyde (PMF) Resin

The resins were prepared by a reported procedure.^{13,14} The PMF resins containing varying amounts of HPM were synthesized by polymerizing varying proportions of phenol and HPM with formaldehyde using oxalic acid as a catalyst at 75°C for 10 h. In a typical experiment for the preparation of PMF-29, a mixture of phenol (20 g, 0.21 mol), HPM (10.8 g, 0.057 mol), and oxalic acid (1.54 g) was heated in a water bath at 75°C. A formaldehyde solution (18.8 mL of a 34% solution, 0.214 mol, for a phenol/formaldehyde ratio of 1: 0.8) was added dropwise under mechanical agitation. After the addition, the contents were stirred at this temperature for 10 h. The resin was dissolved in 100 mL of acetone and precipitated into 1.5 L of a water-methanol (1:1 ratio) mixture. The precipitated polymer was isolated by filtration and purified by repeated precipitation. It was dried at 50°C under a vacuum for 8 h. Characterization was done by spectral and elemental analyses. The molecular weight was determined by GPC, which also confirmed the absence of unreacted monomers in the polymer. For preparing the copolymers PMF-19, PMF-29, and PMF-42 (Table I), the weight percent of HPM (in the phenol mixture) in the feed was varied as 20, 35, and 50%, respectively.

Synthesis of Novolac Resin (PF)

The novolac resin used in this study was prepared by reacting phenol and formaldehyde (taken in a 1:0.8 molar ratio) in the presence of 5% by weight of oxalic acid at 85°C for 8 h. The formed resin was washed several times with boiling water to remove the impurities and unreacted phenol. Water was removed under a vacuum at about 100°C. The polymer was dissolved in methanol and then

	Weight of HPM	Average Functionality		Molecular Weight by GPC			
Reference	in the Polymer (%)	Imide	OH	M_w	M_n	$M_p{}^{ m a}$	$\frac{\text{Dispersity}}{M_w/M_n}$
PF	0	0	7.3	3220	770	3650	4.2
PMF-19	19	1.1	10.0	5800	1170	3570	5.0
PMF-29	29	1.6	9.0	5860	1110	2520	5.3
PMF-42	42	2.2	7.9	6510	1040	2440	6.3

Table I	Characteristics	of the	PMF	and PF	Resins

^a Molecular weight corresponding to peak in GPC.

fractionated using water as a nonsolvent. The second fraction formed in about 40% yield was isolated and dried under a vacuum at 100°C and was characterized by GPC.

Adhesive Preparation and Curing

The 50% solution in MEK of the phenolic resin or its blend with the epoxy resin was applied uniformly as a thin layer over the aluminum substrate. The solvent was allowed to evaporate by keeping the specimens in a hot-air oven at 75– 80°C for about 2 h. They were then cooled to room temperature and assembled together for testing the adhesive properties. Curing at the desired temperature was carried out in a hot-air oven and a pressure of approximately 0.5 MPa was applied over the bonded specimens using a lever-press assembly.

Testing of Adhesive Properties

Lap shear strength (LSS) and T-peel strength were determined using a chromic acid-etched, B-51-SWP aluminum substrate as per ASTM D-1002 and D-1876 methods, respectively. The bonded specimens were tested in an Instron UTM Model 4202, at a crosshead speed of 10 mm/min. For determining the LSS at higher temperatures, the specimens were soaked for 10 min at the desired temperature and then tested at that temperature.

Preparation of Unidirectional (UD) Composite

The UD composites were made using E-glass fibers as reinforcement. A calculated number of tows of the glass fiber were impregnated with a solution of the reactants in MEK and dried at 50° C in a vacuum. The strands were then compressed into 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 dimension for dynamic mechanical analysis (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 \times 6 \times 1 mm. The ILSS of the composites was determined as per ASTM D-2344 in an Instron UTM Model 4202 at a crosshead speed of 1.3 mm/min using specimens of size 30 \times 6 \times 3 mm.

Physical Properties

IR spectra were taken in an FTIR Model Nicolet 510P. Gel permeation chromatography (GPC) analysis was performed on a Waters GPC Model Delt. prep. 3000 using THF as an eluent and with a DRI-R 401 refractive index and UV (at 254 nm) detectors. Polystyrene standards were used for calibration. Elemental analyses were performed using a Perkin–Elmer 2400 elemental analyzer. DMA was performed using a DuPont DMA-983 in a nitrogen atmosphere at a frequency of 1 Hz.

Thermal Properties

The cure characteristics of the resins were studied by DSC using a Mettler TA 3000 system at a heating rate of 10°C/min over the temperature range from 30 to 300°C. Thermogravimetric analysis was performed on a DuPont 990 thermal analyzer in conjunction with a 951 thermogravimetric analyzer in a nitrogen and air atmosphere at a heating rate of 10°C/min over the temperature range from 30 to 700°C.



PMF-EPN CURED NETWORK

Scheme 1 Mechanisms of cure reactions of PMF resin.

RESULTS AND DISCUSSION

Adhesive Properties of Self-cured PMF Resin

The synthesis and characterization of the PMF resins were described elsewhere.^{12–14} Three grades of PMF resins with varying maleimide content, as given in Table I, were used in this study. The maleimide group present in the PMF resin is capable of thermal polymerization to give rise to thermally stable structures as shown in Scheme 1, while the phenolic hydroxyl group can be served to react with active electrophiles to induce secondary curing, such as the ring opening of epoxy.

DSC analysis showed that the curing of PMF occurred in two steps (Fig. 1, curve a): The first step with $T_{\rm max}$ at 170°C is attributed to the condensation of residual methylol groups present in PMF. It was determined that the

resin possesses a small concentration of methylol groups on the imide ring of HPM as indicated in Scheme 1.^{12,14} Since its concentration is very small (nearly 4–7 wt % of the resin as estimated from the mass loss in TGA of the uncured resin at this curing temperature), its presence does not essentially alter the additioncure nature of the resin. The second step is the polymerization of maleimide which starts at 225°C with $T_{\rm max}$ at 270°C. The minor methylol condensation reaction is helpful for early gelation of the system and for avoiding its melt flow at higher cure temperatures.

PMF resins, when self-cured, provided very low values of the LSS and *T*-peel strength. Results of the LSS tested at ambient and at higher temperature (150°C) for a typical resin, PMF-29 (with 29 wt % of hydroxyphenylmaleimide), when cured under different conditions are given in Table II.



Figure 1 DSC of the various resin systems: (a) PMF-29 before cure; (b) PMF-29/EPN before cure; (c) PF/EPN before cure; (d) PMF-29/EPN after cure at 170°C/30 min and 200°C/30 min; (e) PF/EPN after cure at 170°C/30 min and 200°C/30 min; (f) isothermal DSC of PMF-29/EPN at 170°C. Heating rate for dynamic DSC: 10°C/min.

The LSS and *T*-peel strength values are generally poor. The poor adhesive properties of PMF are due to their rigid and brittle crosslinked structures. However, enhancing crosslinking at higher cure temperatures improved the LSS values. Interestingly, the values tend to increase on heating the joints, due probably to thermally induced molecular relaxations in the tightly crosslinked network resulting in a remarkably high retention of LSS at 150°C. The *T*-peel strength values were, however, very poor under all the cure conditions. The extent of maleimide polymerization, extrapolated from results of the studies on the model compound (i.e., *p*-hydroxyphenylmaleimide, see later) cured under identical conditions is also included in the table.

Cocuring with Epoxy Resin

To derive useful adhesives, the PMF resins were used in combination with commercial epoxy resins, making use of the OH–epoxy cure reaction. Epoxy resins dominate the field of structural adhesives, providing good adhesion to metallic substrate. They have good wetting characteristics and provide a void-free glue line upon cure. Epoxy–phenolics are also known to be good hightemperature resistant adhesives.¹⁷ The presence of maleimide groups and their curing in the present case could alter the adhesive characteristics of the system. Accordingly, the adhesive properties of PMF cocured with different grades of epoxy resins were evaluated.

Cure Optimization

The 1:1 blend of PMF and EPN (equivalent ratio based on -OH/epoxy contents) showed the twostage curing in DSC (Fig. 1, curve b) and the possible cure reactions are depicted in Scheme 1. In this case, in addition to the self-cure reactions of PMF, the OH-epoxy reactions (both phenolic and alcoholic -OH) also take place. The DSC of the PF/EPN blend (Fig. 1, curve c) shows that the OH-epoxy reaction starts at about 160°C, with a peak maximum at 250°C. So, in the case of the PMF/EPN blend, it can be considered that the methylol condensation and OH/epoxy reactions occur almost simultaneously. Isothermal DSC of the sample taken at 170°C (also shown in Fig. 1, curve f) showed that these cure reactions were completed in about 20 min. This was further confirmed by IR spectra of the PMF/EPN system taken after an initial cure at 170°C for 30 min.

Postcure Temperature (°C)	Extent of Maleimide Polymerization (%)	LSS at RT (MPa)	LSS at 150°C (MPa)	Retention of LSS at 150°C (%)
200	37	2.1 4.1 4.6	3.5	167
225	75		6.8	166
250	89		9.1	198

Table II Effect of Postcure on LSS of PMF-29

Initial cure: 170°C/30 min. Postcure time: 30 min.

Postcure Temperature (°C)	Extent of Maleimide Polymerization (%)	LSS at RT (MPa)	LSS at 150°C (MPa)	Retention of LSS at 150°C (%)	<i>T</i> -peel Strength at RT (kN/m)
185	12	15.7	5.3	34	0.31
200	37	17.0	14.3	84	0.56
225	75	12.7	13.0	102	0.26
250	89	11.0	13.0	118	0.17

Table III Dependency of Adhesive Properties of PMF-29/EPN (1:1) on Postcure Temperature

Initial cure: 170°C/30 min; postcure time: 30 min.

The disappearance of the epoxy peak at 905 cm^{-1} confirmed the completion of the OH/epoxy reaction within this time. Hence, the adhesive compositions were subjected to two-step curing, first at 170°C for 30 min and then a further cure of 30 min each at temperatures 185, 200, 225, and 250°C. The DSC curves of PMF/EPN and PF/EPN after cure at 170°C/30 min followed by postcure at 200°C/30 min are presented in Figure 1 (i.e., curves d and e, respectively). It can be seen that under these cure conditions PF/EPN is completely cured, whereas a residual cure exotherm is present in the case of PMF/EPN, which indicated the incomplete polymerization of maleimide groups under this cure schedule (for more discussion, see later).

The adhesive properties, obtained for PMF-29 when cocured with EPN under the different cure conditions, are given in Table III. Optimum LSS and T-peel properties were obtained for the system postcured at 200°C for 30 min. Since the first two stages are completed in the initial cure for all systems, the variation in properties should be arising from the different extents of crosslinking through the maleimide polymerization. Curing at higher temperature is expected to promote maleimide polymerization. The imide polymerization is usually associated with only small heat changes and, hence, its monitoring by DSC is often not dependable. IR spectra did not give a quantitative picture of the extent of polymerization of maleimide due to the overlap of many other absorptions with its characteristic bands. Hence, an attempt was made to estimate the extent of polymerization of maleimide in PMF by following the thermal homopolymerization of the model compound, HPM, cured at these four temperatures and for different time intervals at 200°C. The extent of polymerization was calculated from the GPC analyses of the polymer mixture by estimating the area of the chromatograms

for the monomer and polymer of HPM by manual deconvolution. Typical GPC traces for the polymerization of HPM done at different temperatures are shown in Figure 2 and the conversion details for different temperatures and time are given in Table IV. The extent of polymerization naturally increases with the time and temperature, and at 200°C/ 30 min, it corresponds to 37%.

Kinetics of Polymerization of HPM

Assuming a first-order reaction for the polymerization of HPM, the data could be treated kinetically. For isothermal polymerization, the kinetic equation is

$$d\alpha/dt = k(1 - \alpha) \tag{1}$$



Figure 2 GPC traces of HPM polymerized for 30 min at (a) 185°C, (b) 200°C, (c) 225°C, and (d) 250°C.

al at 200°C	Varying Temperature for 30 Min			
Conversion	Temperature	Conversion		
(%)	(°C)	(%)		
37	185	12		
62.5	200	37		
66	225	75		
	al at 200°C Conversion (%) 37 62.5 66 78	Al at 200°CVarying TemperaConversion (%)Temperature (°C)37185 62.566 66 78225 250		

Table IV Variation in Extent of Polymerization of HPM with Time and Temperature

Integrating the equation,

$$\ln(1-\alpha) = -kt \tag{2}$$

where α is the fractional conversion at time *t*, and *k*, the rate constant at 200°C. A plot of $\ln(1 - \alpha)$ against *t* gave a reasonably good straight line from the slope of which *k* was obtained as 0.0121 min⁻¹.

By treating the conversion data obtained at various temperatures for a fixed duration of 30 min by the Arrhenius method,

$$\ln(1-\alpha) = -Ae^{-E/RT}t \tag{3}$$

when t is constant. Therefore,

$$\ln\{-\ln(1-\alpha)\} = \ln(A \ t) - E/RT$$
 (4)

A plot of $\ln\{-\ln(1 - \alpha)\}$ against I/T gives a straight line with a slope equal to -E/R and an intercept equal to $\ln(A \times t)$. Both these plots are shown together in Figure 3. The activation energy (E) works out to be 86.5 kJ/mol and A equals 4.04 $\times 10^7 \text{ min}^{-1}$. The rate constant at 200°C calculated back from the Arrhenius constants works out to be 0.0114 min⁻¹ as against the experimental value of 0.0121 min⁻¹ obtained from the isothermal polymerization. The two results are in mutual agreement.

Extrapolating these results to the PMF/EPN system, it is to be concluded that a higher extent of crosslinking through the polymerization of maleimide groups embrittles the system, reducing the absolute values of the LSS and *T*-peel, but is conducive for better property retention at 150°C (see Table III). The effect of the cure temperature on the percent retention of the LSS at higher temperatures is compared with conversion of maleimide in Figure 4. The increase in the LSS values at 150°C for the system cured at 250°C fur-

ther substantiates that the reduction in the property at ambient temperature with increase of cure temperature is due to the embrittlement of the system. For the system with maximum crosslinks, secondary relaxation of the imidophenolic moiety induced at high temperature leads to enhancing the properties at this temperature. Since the optimum adhesive properties were obtained for the cure schedule of 30 min at 170°C followed by a postcure of 30 min at 200°C, this schedule was adopted for further systems.

Effect of Imide Concentration on Adhesive Properties

In one set of experiments, the three PMF resins with a hydroxyphenylmaleimide content of 19, 29, and 42% by weight were mixed with EPN, taken in a 1 : 1 OH/epoxy molar ratio and cured as above. The LSS at different temperatures and T-peel strength at ambient temperature are com-



Figure 3 Kinetic plots for polymerization of HPM: (■) isothermal at 200°C; (▲) Arrhenius plot.



Figure 4 Dependency of (\bullet) LSS retention at 150°C and (\blacksquare) extent of HPM polymerization on cure temperature.

piled in Table V. It is found that maximum adhesive properties at room temperature are obtained for the system containing a moderate maleimide concentration (i.e., PMF-29). A too low or too high concentration of the imide is found not desirable (under the cure conditions employed here) since the crosslink density is less in the former and too high in the latter. Also, PMF- 42, being the most brittle, provides the lowest LSS and T-peel strength at RT. This trend may be different under different cure conditions. Further studies were, hence, limited to the PMF-29 resin. Compared with a novolac resin (PF), it is found that a small concentration of imide practically unaffects the properties both at ambient and at high temperature and that a moderately high concentration of imide is desirable for optimum properties. The presence of imide groups is particularly helpful for enhancing the high-temperature retention of the adhesive properties.



Figure 5 Effect of phenol/epoxy stoichiometry on LSS and *T*-peel strength: (■) LSS at RT; (●) LSS at 150°C;
(▲) LSS at 175°C; (◆) *T*-peel strength at RT.

Effect of Epoxy–Phenol Stoichiometry

The epoxy/hydroxyl(phenolic) stoichiometry was varied to study its effect on the adhesive properties. The results obtained for the PMF-29/EPN system are shown in Figure 5. The adhesive strength becomes optimized at a 1:1 equivalent both for LSS and T-peel. LSS at 150 and 175°C also becomes optimized at this stoichiometry. This is a direct consequence of the crosslinking arising from the OH/epoxy reaction. The 1:1 stoichiometry ensures maximum crosslinking through the OH/epoxy reaction. Unlike in the case of maleimide, a maximum extent of phenolepoxy cure is desirable for promoting better adhesion and for its better retention at high temperature. An excess of EPN leaves unreacted epoxy groups, leading to plasticization, which causes diminution of properties. Although their absolute values were lower, the phenol-rich systems exhibited a better high-temperature retention of prop-

Table V	Adhesive	Properties	of Variou	s PMF	Resins	Blended	with	EPN
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System	LSS at RT (MPa)	LSS at 150°C (MPa)	Retention of LSS at 150°C (%)	LSS at 175°C (MPa)	Retention of LSS at 175°C (%)	<i>T</i> -peel Strength at RT (kN/m)
PF/EPN	15.5	7.2	47	3.1	20	0.40
PMF-19/EPN	15.3	5.6	37	2.8	18	0.43
PMF-29/EPN	17.0	14.3	84	8.0	47	0.56
PMF-42/EPN	11.3	8.2	73	3.9	35	0.08

Cure: 170°C/30 min and 200°C/30 min.

System	OH : Epoxy Ratio	LSS at RT (MPa)	LSS at 150°C (MPa)	Retention of LSS at 150°C (%)	<i>T</i> -peel Strength at RT (kN/m)
PMF/EPN	1:1	17.0	14.3	84	0.56
PMF/GY-250	1:0.5	10.3	8.3	81	0.16
PMF/GY-250	1:1	12.0	3.0	25	0.11
PMF/GY-250	1:1.5	11.0	1.9	17	Very poor
PMF/CT-200	1:1	3.2	0.5	15	Very poor

Table VI Comparison of Adhesive Properties of PMF-29 Blended with Different Epoxy Resins

Cure schedule: 170°C/30 min and 200°C/30 min.

erties thanks to the presence of thermally stable imido-phenol groups in the network.

Dependency of Nature of Epoxy Resin

In another part of this study, various epoxy resins were used as a curative for PMF-29 and the comparative adhesive properties are listed in Table VI. In the case of GY-250 with a moderately high epoxy value, the OH/epoxy ratio was also varied. It was found that the LSS and *T*-peel strength at RT become optimized for a 1 : 1 ratio in this case also, but the retention of the LSS at high temperature decreases with decrease in PMF content (i.e., increase in epoxy content). The adhesive properties are very poor for the high molecular weight epoxy resin, CT 200, whose epoxy content is very low. For a fixed reactant ratio of 1 : 1, the adhesive properties at RT diminish proportionately as the epoxy content of the epoxy resin decreases. In the latter two cases, crosslink density and novolac content are proportionately less and the concentration of polar groups is also less. These factors also appear critical in determining the adhesive properties. It may be remarked that T-peel strength decreases systematically as the curative shifts from EPN to CT-200 with a proportionately reduced epoxy content. The latter systems are expected to be more flexible and tougher and, thereby, they are expected to contribute to the peel strength. However, it appears that the reduction in primary bonding itself impairs the adhesion.

Thermoadhesive Profile

From the above studies, it was concluded that the resin formulation of PMF-29 with EPN in a 1:1 ratio gives the optimum adhesive properties with 84 and 47% retention of the LSS at 150 and 175°C, respectively, and that it can serve as a

structural adhesive for moderately load-bearing applications. For comparative evaluation, a novolac resin (PF) was used in the place of PMF-29 and the comparative temperature dependency of the LSS is given in Figure 6. The superiority of the imide functional one as regards the adhesive properties at ambient conditions and their retention at high temperature is evident from this figure. The effect of imide is manifested particularly in a better thermoadhesive property profile.

Dynamic Mechanical Analysis (DMA)

To ascertain the role of the imide groups in enhancing the thermoadhesive profile of the system, DMA of the cured PMF/EPN and PF/EPN systems was performed. Since the cured neat resins were quite brittle, they were examined as their unidirectional composite with glass fiber. The



Figure 6 Thermoadhesive profile of cured systems: (■) PMF-29 /EPN; (●) PF/EPN.



Figure 7 DMA of UD composites: (a) PMF/EPN-200°C; (b) PF/EPN/200°C; (c) PMF/EPN/225°C. (a')–(c'): tan δ curves corresponding to (a)–(c).

comparative analyses are shown in Figure 7. Since the resin content in the two composite systems could not be maintained exactly the same, the comparison was made between the temperature profile of the percent retention of the dynamic storage modulus (E'). It is found that both the PMF/EPN and PF/EPN systems cured under the optimized cure schedule do not essentially show any difference in their DMA pattern. Both exhibited the tan δ maximum at around 160°C, corresponding to their T_g 's. Thus, the small extent of additional cure induced through the imide groups has not resulted in altering the thermomechanical profile. However, curing the PMF/ EPN system at a higher temperature (225°C) results in a shift of the T_g to 176°C. However, the resin cured at this temperature was found to be very brittle and, consequently, with poor adhesive properties. The difference in behavior of the maleimide-functional system in DMA and in the thermoadhesive analysis implies that the superior thermoadhesive profile of the PMF/EPN system must not necessarily be arising from the cor-



Figure 8 TGA of (a) PMF/EPN in N_2 , (b) PF/EPN in N_2 , (c) PMF/EPN in air, and (d) PF/EPN in air. (a')–(d') are corresponding DTG curves.

responding improvement in mechanical strength. On the other hand, it is contributed through the secondary forces induced by the polar imide groups. The partial polymerization of the imide helps consolidate these secondary forces of attraction both within the resin system and at the interphase. The enhanced bonding characteristics of the PMF-based system was also manifested in better interlaminar shear strength of the UD composite based on it (ILSS = 85.5 MPa) as against that of the PF-based one (ILSS = 68.5 MPa). In other words, the PMF system ensures a stronger adherend-adhesive interphase.

Thermal Analysis

Earlier studies have shown that the thermal stability of the PMF resin is superior to that of thermally crosslinked resoles.¹² Hence, it was of interest to study the thermal stability of the epoxycured PMF resin. The thermograms in nitrogen and air of PMF-29/EPN and PF/EPN are shown in

Table VII Thermal Decomposition Data of PMF-29/EPN and PF/EPN Systems

System	TGA Atmosphere	T_i (°C)	T_p (°C)	T_e (°C)	Residue at $T_e_{(\%)}$	Residue at 700°C
PMF/EPN	Nitrogen	300	440	570	53	44
PF/EPN	Nitrogen	300	440	570	45	39
PMF/EPN	Air	300	427	500	55	0
PF/EPN	Air	300	417	500	46	0

Figure 8 and the relevant data on the initial decomposition temperature (T_i) , peak decomposition temperature (T_p) , pyrolysis end temperature (T_e) , and residues at the end of pyrolysis and at 700°C are given in Table VII. In nitrogen, both systems decompose in a single stage and the thermograms are nearly identical as regards the T_i , T_{p} and T_{e} values but the char residue is substantially enhanced by the presence of the imide groups. In air, the decomposition occurs in two stages: The first one corresponds to the pyrolysis, and the second one, to the oxidative decomposition of the residue. Here, also, both systems behave identically as regards their initial decomposition pattern but with an enhanced char residue for the PMF-based one at higher temperature. Generally, the presence of imide groups reduced the rate of thermal erosion at higher temperature, leaving more char residue at a given temperature.

CONCLUSIONS

Maleimide-functional novolac-phenolic resin cured by the novolac-epoxy resin, through a combination of epoxy/phenol reactions and maleimide polymerization, results in an adhesive formulation with better adhesive properties than those of similarly cured conventional novolac. The optimum properties are achieved for the formulation containing a stoichiometric combination of phenol and epoxy functions. The adhesive properties are better when the epoxy content of the epoxy curative is higher. The superiority of the imido-phenolic resin to the conventional novolac is reflected particularly in a better thermoadhesive profile. The adhesive properties are optimized for moderate crosslinking through the imide function. The improvement in properties of this system results mainly from the consolidation of the secondary forces of attraction induced by the polar imide groups through its partial polymerization. The study implies that the completion of epoxy-phenolic reaction and moderate crosslinking through the maleimide polymerization is conducive for achieving optimum adhesive properties.

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