

Addition-Cure-Type Phenolic Resin Based on Alder-ene Reaction: Synthesis and Laminate Composite Properties

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ABSTRACT: A maleimide-functional phenolic resin was reactively blended with an allyl-functional novolac in varying proportions. The two polymers were coreacted by an addition mechanism through Alder-ene and Wagner–Jauregg reactions to form a crosslinked network system. The cure characterization was done by differential scanning calorimetry and dynamic mechanical analysis. The system underwent a multistep curing process over a temperature range of 110–270°C. Although the cure profiles were independent of the composition, the presence of maleimide led to a reduced isothermal gel time of the blend. Increasing the allylphenol content decreased the crosslinking in the cured matrix, leading to enhanced toughness and improved resin-dominant mechanical properties of the resultant silica laminate composites. Changing the reinforcement from silica to glass resulted in further amelioration of the resin-reinforcement interaction, but the resin-dominant properties of the composite remained unaltered. Increasing the maleimide content resulted in enhanced thermal stability. Integrating both the reactive groups in a single polymer and its curing led to enhanced thermal stability and T_g , but to decreased mechanical properties of the laminate composites. This can be attributed to a brittle matrix resulting from enhanced crosslinking facilitated by interaction of the reactive groups located on the polymer of an identical backbone structure. The cured polymers showed a T_g in the range of 170–190°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 737–749, 2001

Key words: addition-cure phenolics; maleimide-functional phenolics; allyl-functional phenolics; reactive blending, Wagner–Jauregg reaction; Alder-ene reaction; polymer matrix composites

INTRODUCTION

Despite possessing high-temperature resistance, the inherent brittleness and evolution of volatiles during a condensation cure have been the major obstacles for application of conventional phenolic resins in several important engineering areas. The brittleness can be obviated through toughening with thermoplastics or rubber,^{1,2} although it might lead to reduced thermal stability. The con-

densation cure can be avoided by designing phenolic resin possessing addition-curable groups that are also thermally stable. Addition-curable phenolic resins could be the answer to many drawbacks of conventional phenolics, particularly with regard to countering the processing problems associated with the evolution of volatiles during curing.^{3,4} Two recent reviews brought forth the advances made in phenolic resins including those in addition-curable phenolics.^{5,6} In such systems, the addition-curable groups are selected to be thermally stable, so that the thermal characteristics of the resultant network are not adversely affected. We reported a few such sys-

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tems including a maleimide-functional novolac with improved thermal stability, which also provided good mechanical properties to its composites.⁷⁻⁹ The thermal curing of the system through polymerization of the maleimide group, however, rendered the systems brittle. This is because of the presence of polymaleimide entities, which are known to be brittle.¹⁰⁻¹² As a result, the mechanical properties of the resultant composites did not improve significantly over the conventional phenolic resins.⁹

Bismaleimides are toughened by reactive blending with diallyl bisphenols. The coreaction takes place by an Alder-ene reaction^{13,14} through an intermediate Wagner-Jauregg reaction step.¹⁵ The cure reaction in such systems results in the formation of crosslinked cyclic structures. This is expected to impart toughness to the matrix without sacrificing the thermal characteristics considerably. Several polymer systems based on the reaction of allylphenols and bismaleimides are known.^{14,16-18} There have been some patent claims on blends of allylphenol-based novolac and bismaleimides.^{19,20} We report here an addition-cure phenolic resin system based on the coreaction of maleimide-functional novolac with an allyl-functional one. This article focused on their synthesis and reactive blending. The cure characterization and related processes are discussed. The thermal stability of the cured blends and mechanical properties of laminate composites of the system were also evaluated.

EXPERIMENTAL

Materials

Phenol (CDH, Agra, India), formaldehyde supplied as a 34% by weight aqueous solution (Sisco Research, Mumbai, India), 4-aminophenol (E-Merck, Germany), and P₂O₅ (SD Fine Chemicals, Mumbai, India) were used as received. Maleic anhydride (CDH) was purified by sublimation. Allylphenol (E-Merck) was used as received. Dimethylformamide (DMF; Qualigens, Mumbai, India) was distilled from P₂O₅. All other solvents were of reagent grade and were used without further purification. Silane-treated, plain-weave E-glass of 0.175 mm thickness (Unnathi Corp., Ahmedabad, India) and 8 harness satin weave, 0.5-mm-thick silica cloth (Valeth High Temperature Composites, Madras, India) were used as reinforcements. *N*-(4-hydroxyphenyl)maleimide

(HPM) was synthesized in the lab by a known procedure.²¹

Instruments

FTIR spectra were recorded with a Nicolet 510 P instrument. The cure characteristics of the resins were studied by DSC using a Mettler DSC-20 analyzer at a heating rate of 10°C/min in a nitrogen atmosphere. Thermogravimetric analysis was performed on a DuPont 2000 thermal analyzer in conjunction with a 951 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 10°C/min. NMR spectra were recorded with a JEOL FX 90 MHz spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a Waters GPC Model Delta Prep. 3000 using THF as the eluent and with 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 Model 2400 elemental analyzer. Dynamic mechanical analysis (DMA) was carried out using a DuPont DMA-983 in a nitrogen atmosphere at a frequency of 1 Hz. Single-ply prepreg was used for DMA analysis of the resin. For composites, specimens of dimension 60 × 12 × 2 mm³ were used. The fracture surface of the composites was analyzed by a Hitachi S-2400 Model scanning electron microscope (SEM) having a resolution of 4 nm with an accelerating voltage of 25 kV and an ultimate vacuum of 10⁻⁷ Torr. Gold coating was done in an ion sputter coater, Hitachi Model E101, using a gold-palladium alloy.

Synthesis of Phenol-Hydroxyphenyl(maleimide)-Formaldehyde (PMF) Resin

The PMF resin was synthesized by copolymerizing phenol (65 g, 0.69 mol), HPM (35 g, 0.19 mol), and formaldehyde (57.5 mL, 34% formalin, 0.70 mol) using oxalic acid (5% by weight of phenols, 5 g) as a catalyst at 75°C for 10 h. The reaction mixture was diluted with 200 mL of acetone and the polymer was precipitated into a water-methanol (40% methanol) mixture. The resin was purified by repeated precipitation using the same solvent-nonsolvent system. The filtered polymer was dried at 50°C under vacuum for 8 h. Characterization was done by spectral and elemental analyses. Molecular weight was determined by GPC, which also confirmed the absence of unreacted monomers in the resin. Characterization was also done by proton NMR. ¹H-NMR showed

signals due to aromatic protons at 6.75–7 ppm and those due to the $-\text{CH}_2-$ groups at 3.88 ppm. Minor signals were observed at 4.53–4.66 ppm, attributable to uncondensed methylol groups formed on HPM.⁸

Synthesis of Phenol-Allylphenol-Formaldehyde (PAF) Resin

PAF resin was synthesized in a similar way, by reacting phenol (60 g, 0.64 mol), allylphenol (40 g, 0.30 mol), and formaldehyde solution (64.9 mL, 34% solution, 0.75 mol) in the presence of oxalic acid (5 g) at 75°C for 10 h. The polymer was purified by repeated precipitation in a methanol-water (35% methanol) mixture and dried under vacuum at 50°C. The composition of the purified polymer was determined by ¹H-NMR. The ¹H-NMR spectrum of the PAF resin showed signals due to $=\text{CH}_2$ (broad, 5 ppm), $=\text{CH}$ (m, 6 ppm), and $-\text{CH}_2$ (d, 3.47 ppm). Methylene bridges and aromatic protons appeared at 3.90 and 6.90 ppm, respectively.

Synthesis of Phenol-Maleimidophenol-Allylphenol-Formaldehyde (PMAF) Resin

Phenol (56.7 g, 0.60 mol), maleimidophenol (35 g, 0.18 mol), and allylphenol (8.3 g, 0.07 mol) were polymerized with formaldehyde (55.8 mL, 34% formalin, 0.69 mol) in the presence of oxalic acid catalyst (5% by weight). Allylphenol was taken in such a way that the allylphenol:maleimide molar ratio became 1:3. The reaction was continued for 10 h under stirring at 75°C. The polymer was purified and characterized as above. Its composition was determined by elemental analysis and proton NMR.

Blending and Curing

Blending of the polymers was done by dissolving weighed quantities of PMF and PAF resins together in methyl ethyl ketone (MEK) and evaporating the solvent under a vacuum at 50°C. The blends were cured by heating them in vacuum at 250°C for 2 h.

Determination of Sol Content:

The sol content was determined by swelling the cured polymer in THF for 4 days and determining the weight of the soluble and or insoluble part by extracting them with the same solvent.

Determination of Gel Time

Gel time of the blends at 150°C was determined by heating about 1 g of the resin, taken in a test tube, immersed in a thermostated oil bath, and visually monitoring the viscosity of the resin using a glass thermometer. The time at which the resin ceases to flow is determined as the gel time. The error in this determination was roughly 5%.

Preparation and Testing of Composites

Silica/glass cloth was impregnated with the MEK solution of the resin and dried at room temperature for 18 h. It was cut into pieces of dimension $12 \times 10 \text{ cm}^2$, stacked, and molded in a hydraulic press between thick metallic sheets to achieve the proper number of plies and thickness. The prepreg was heated initially at 100°C for 30–45 min (depending on the composition) to achieve sufficient viscosity and tackiness. The curing of the composites was done as per the following programmed heating schedule: A pressure of 200 psi was applied after gelation of the system at 100°C and was maintained throughout the process.

	Temperature (°C)			
	100	150	200	250
Time (min)	30	60	60	60

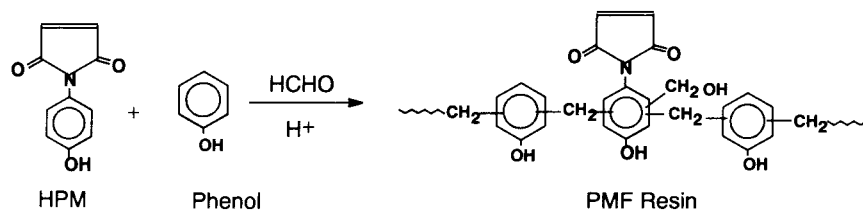
Specimens, cut from the slabs, were tested for mechanical properties using an Instron universal testing machine, Model 4202, in accordance with the following ASTM testing standards—flexural strength: ASTM D 790; compressive strength: ASTM D 3410; and interlaminar shear strength (ILSS): ASTM D 2344.

Resin Content

The resin content was determined by heating the specimens in air at 800°C for 4 h and estimating the mass loss. The resin content was approximately 25–30% by weight.

RESULTS AND DISCUSSION

In a previous article, we reported the syntheses of maleimide-functional phenolic resins (PMF) which undergo curing principally by addition polymerization of the maleimide groups.⁸ The resin was found to possess a very small fraction (less



Scheme 1 Synthesis of PMF resin.

than 5% by weight) of condensable methylol groups located on the phenyl ring of maleimido-phenol as depicted in Scheme 1. The PMF resin obtained through copolymerization of phenol, HPM, and formaldehyde was found to be thermally more stable and the composites derived from them possessed better mechanical properties in comparison to the conventional phenolic resins.⁹ However, the brittle nature of the cured resin limited the mechanical properties of the resultant composites. Brittleness arises from the crosslinks caused by the rigid maleimide groups. Maleimides can be toughened by reaction with allylphenols via an Alder-ene reaction (Wagner–Jauregg reaction).^{14,16–18} Hence, in this work, the maleimide-functional novolac was reactively blended with an allylphenol-based novolac and the properties of the blend were evaluated.

The maleimide-functional phenolic resin (PMF resin) was obtained by polymerizing a mixture of HPM and phenol with formaldehyde. Its characterization was described in detail in a previous article.⁸ The synthesis and structure of the polymer are shown in Scheme 1. The polymer contained 29% by weight of hydroxyphenyl(maleimide) groups. Allylphenol novolac (PAF) was obtained by copolymerizing allylphenol and phenol with formaldehyde. It was characterized by NMR, IR, and GPC. A novolac containing 40% of allylphenol was made. The composition of the PAF resin was determined by proton NMR. The novolac copolymer of allylphenol with phenol was

made such that the allyl groups are statistically sufficiently spaced in the novolac. The characteristics of the two polymers are included in Table I. The FTIR spectrum of the PAF resin showed the characteristic absorption of the allyl function at 913 cm^{-1} , in addition to other absorptions, confirming the incorporation of allylphenol in the polymer backbone. The composition of the PMF resin was determined by elemental analysis and characterized further by IR and GPC.⁸

Reactive Blending and Curing

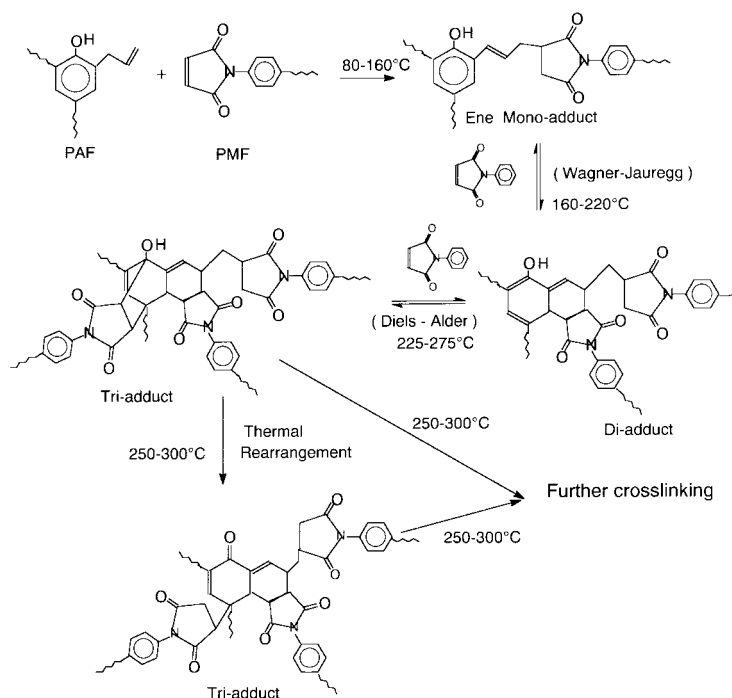
Since maleimides are known to react with allylphenol through an Alder-ene reaction,^{13–16} the same reaction was expected during curing of the blend of PMF and PAF resins. The PMF resin was blended with the PAF resin in varying proportions such that the molar ratio of maleimide to the allyl function varied from 5:1 to 1:1. The expected reaction sequences and mechanisms are depicted in Scheme 2 (see discussion below). This mechanism was confirmed by recent studies on model compounds.¹³ Spectral analysis confirmed that the PMF resin possesses a small proportion of $\text{---CH}_2\text{OH}$ groups (5 wt %) capable of undergoing a condensation reaction about $150\text{--}170^\circ\text{C}$, thereby causing an early gelation of the blends containing PMF.

The cure characteristics of these blends were studied by DSC. The DSC analysis of the PMF resin showed two-stage curing, corresponding to

Table I Characteristics of PMF and PAF Resins

Ref.	Wt % HPM	Wt % Allylphenol	Molecular Weight (GPC)			
			M_p	M_w	M_n	M_w/M_n
PMF	29	0	2520	5860	1110	5.3
PAF	0	40	1040	750	490	1.5
PMAF	18.3	8.3	2490	4530	1170	3.9

M_p , M_n , and M_w are peak, number-average, and weight-average molecular weights.



Scheme 2 Alder-ene reaction mechanism and structure of cured network.

methylol condensation (at 170°C) and maleimide polymerization (at 260°C), whereas that of PAF resin showed a single, broad, weak exotherm with a peak temperature at 270°C due to the polymerization of the allyl group. Under pure thermal conditions, allyl groups are known to polymerize with great difficulty.

DSC of the blends showed mainly three broad exotherms. From literature evidence^{16,18,22} and by comparing the DSC of the neat resins, these exotherms can be assigned as follows: The first exotherm (80–160°C) can be attributed to the “ene” reaction between maleimide and allyl groups. At this temperature, the ene reaction is reported to take place only at a slower rate. The second exotherm (160–220°C) is in the range of the methylol (of the PMF resin) condensation reaction. In this temperature range, the Diels–Alder addition of maleimide to the ene adduct (known as the Wagner–Jauregg reaction¹⁵) is also reported.¹³ The ene reaction could parallelly take place at this temperature at a significant rate. The third exotherm around 225–270°C is due to a Diels–Alder reaction to form a *tris* adduct. It was reported that the Wagner–Jauregg and other Diels–Alder reactions are reversible under these cure conditions.¹³ It is claimed that a *tris* adduct can also rearrange to form a ketone *tris* adduct,

which coexists with its precursor at higher temperature. At this temperature, the polymerization of excess maleimide, ene homopolymerization, and further crosslinking of the *tris* adducts are also possible. Thus, the network structure could be complicated due to a myriad of reactions possible at higher cure temperatures. The possible pathways for the curing reaction are depicted in Scheme 2. As per the established mechanism, an optimum formulation for maximum crosslinking requires allylphenol and maleimide in the molar ratio 1:3. Compositions outside this ratio may undergo additional curing through the thermal homopolymerization of allyl or maleimide groups depending on the composition. The DSC thermograms of the components and of a typical blend (MAP 3) are shown in Figure 1. The similarity of the cure pattern to the published work^{16,18} on similar compounds confirms that the cure mechanism in the present case is similar to the earlier proposed ones. An earlier study indicated the presence of a mild exotherm above 300°C,¹⁸ but this was absent in this case. Parallel studies on the Alder-ene reaction performed in this laboratory have also not given any evidence for such an exotherm.²³ The curves did not show much variation with composition. DSC recommended the final cure temperature of 250°C for the blends

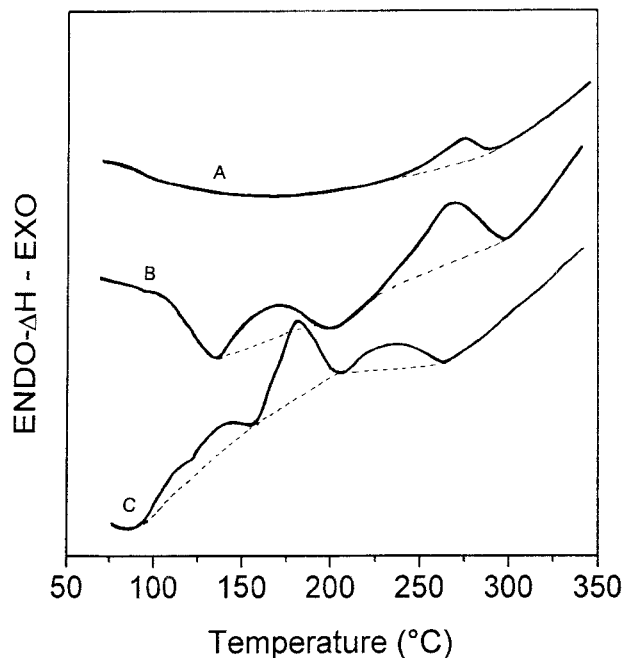


Figure 1 DSC thermograms of blend and its components. (A) PAF; (B) PMF; (C) MAP3; heating rate $10^{\circ}\text{C}/\text{min}$.

and they were cured at this temperature for 2 h. Cure characterization was also done by DMA studies to be discussed later.

Gelation Studies

Normally, thermoset resins are subjected to stagewise curing and systems are gelled at a relatively lower temperature to avoid problems related to rapid cure and melt flow (resin bleeding) at higher temperatures. The gel time was determined for different blend compositions at a typical temperature of 150°C and its composition dependency is shown in Figure 2. Gel time was found to decrease with increase of the maleimide content. This is due to two reasons: The partial gelation caused by the condensation of the methylol groups present in the PMF resin at this temperature can accelerate gelation. The Alder-ene and Diels-Alder reactions leading to crosslinking are facilitated by enhancing the maleimide function and this accounts, principally, for the reduced gel time. The data on the gel time are useful for the processing of a resin and its composites.

The coreaction between maleimide and allyl functions was confirmed by heating the neat resins and a blend separately at 200°C for 2 h under

a vacuum and determining the sol content in each case. The PMF and PAF resins gave 13 and 98.5% soluble parts, respectively, after curing for 2 h at 200°C . The blend used (MAP3) for this study contains 82.2% by weight of the PMF resin and the rest is of the PAF resin, corresponding to a molar ratio of 3:1 for maleimide and allylphenol. A sol content of 28.2% was expected in the absence of any coreaction. The obtained sol content of 9.3% confirmed the coreaction between the two polymers. At higher temperature, a proportion of the coreacted polymer can be expected to be still higher. A lower cure temperature of 200°C was selected for this study to preclude the probability for homopolymerization of PAF and PMF resins (which obviously does not proceed at 200°C). The blends were cured at 250°C for 2 h under vacuum. The cure completion was evident from the complete insolubility of the cured products. It was also confirmed by FTIR and DMA (to be discussed in detail later) studies.

Characterization of Cured Blends

The FTIR spectra of the blend (MAP3) before and after cure are shown in Figure 3. The intensity of absorption due to maleimide carbonyl at 1700 cm^{-1} was found to decrease. On transforming maleimide to succinimide during the polymerization, the absorptivity of the $\text{C}=\text{O}$ peak in the IR spectrum generally decreases by about 50% without any significant change in the frequency of absorption.²⁴ In the present case, the molar absorptivity of the carbonyl groups was found to decrease significantly. This is due to the differ-

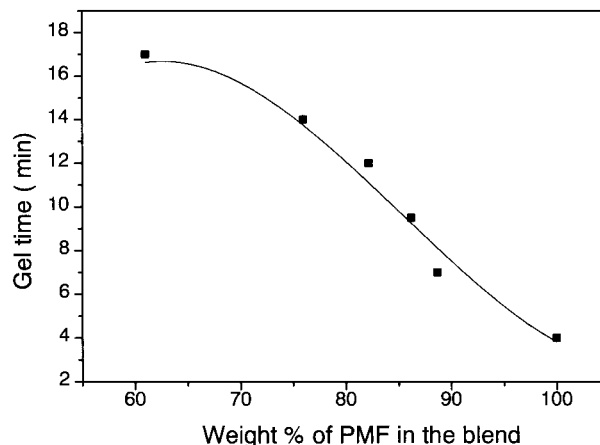


Figure 2 Variation of isothermal geltime at 150°C with blend composition.

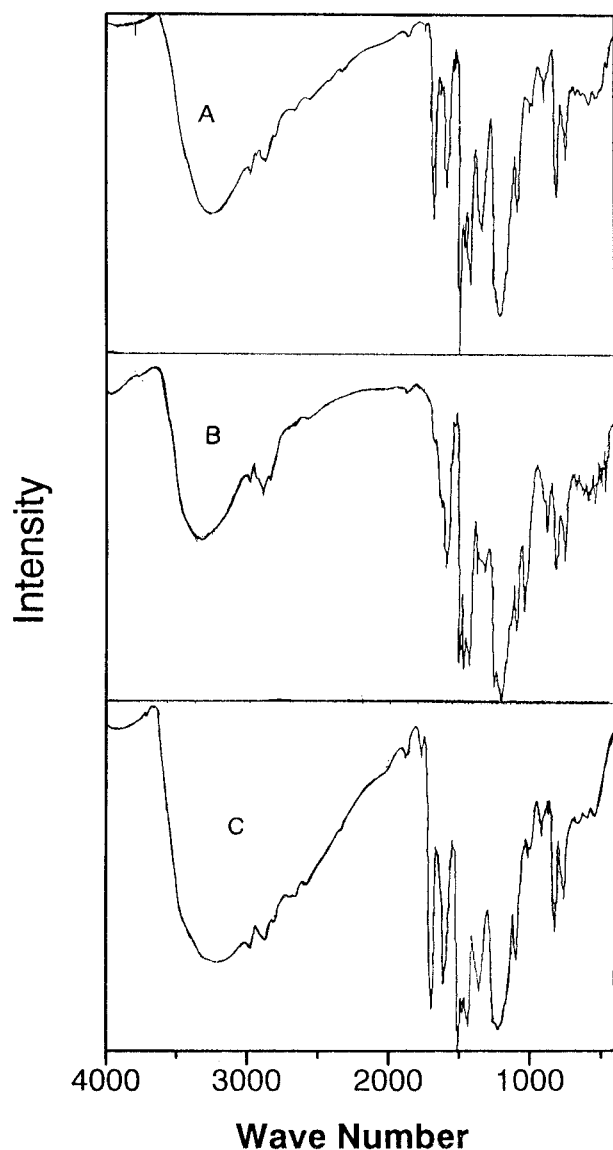


Figure 3 FTIR spectra (KBr): (A) MAP3; (B) MAP3 cured; (C) PMAF.

ence in the mechanism of polymerization of the maleimide groups in the presence of allyl groups, which renders the environment of C=O groups in the cured polymer different from that resulting from the simple addition polymerization of maleimide groups. An additional peak at 1648 cm^{-1} present in the IR of the cured system can be attributed to a C=C stretching vibration of the unsaturated groups generated as a result of the coreaction, which do not undergo facile thermal polymerization.¹³ The absorption due to the C—O stretching of the alcohol formed during curing reaction is observed at 1043 cm^{-1} . These observations confirmed the coreaction of allyl and ma-

leimide functions in league with the established mechanisms, indicated in Scheme 1.

Evaluation as Matrix Resin in Laminate Composites

The PMF resin and blends were evaluated as matrix resins in laminate composites with silica and glass as reinforcements. The prepregs were made by the solution-impregnation process. On heating, the resin was found to soften and develop tackiness around $100\text{--}120^\circ\text{C}$. The cure schedule for making a composite was optimized by DMA.

Cure Characterization of Prepregs by DMA

Since the blend could not be shaped to a DMA specimen, the nonisothermal DMA of the glass prepreg of the blend was performed. The DMA shown in Figure 4 manifested, essentially, a two-stage curing process. The ene reaction detected in DSC in the $80\text{--}160^\circ\text{C}$ range went unnoticed in the DMA, since the glass transition and softening of the blend in this temperature range caused a sharp decrease in the E' property. A corresponding E'' peak in this range is noticeable. Moreover, it has been shown in a recent study that the ene reaction does not give rise to any increase in E' since it does not amount to significant crosslinking.²³ The Wagner–Jauregg reaction detected at $160\text{--}210^\circ\text{C}$ is also reproduced as a step in DMA. This reaction adds to the network buildup. The major networking is via the Diels–Alder reaction and subsequent crosslinking detected in the temperature range of $225\text{--}350^\circ\text{C}$ in DMA. DSC showed this reaction as an exotherm spreading from 225 to 275°C . But DMA shows that the network buildup continues even beyond 350°C under the dynamic heating condition. In fact, DMA shows a tendency for plateau formation for E' at around 275°C . The crosslinking reactions occur-

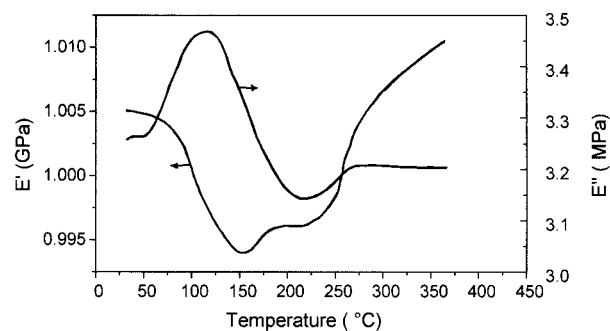


Figure 4 Nonisothermal DMA of MAP3/glass prepreg in nitrogen. Heating rate: $2^\circ\text{C}/\text{min}$, 1 Hz.

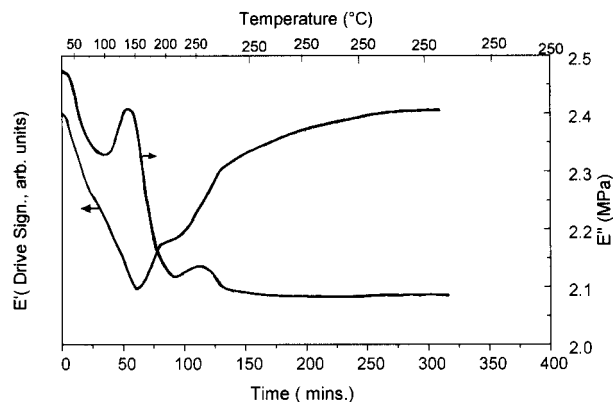


Figure 5 Isothermal DMA of MAP3/glass prepreg at 250°C in nitrogen. Heating rate for dynamic part: 2°C/min, 1 Hz.

ring beyond this temperature must proceed slowly and are not associated with much enthalpy, with the result that this reaction is not sensed by DSC. Minor reactions toward the cure end can give rise to a significant increase in the modulus and are more easily detected in DMA than in DSC.

To optimize the processing of a laminate, isothermal DMA was performed using a prepreg. The prepreg was heated to 250°C at a rate of 5°C/min and maintained at this temperature isothermally. Figure 5 shows that the curing becomes complete after 120 min at this temperature. The buildup in the storage modulus (E') of the resin became almost stagnant after 120 min at 250°C, which indicated the completion of the cure reaction. However, during the composite preparation, the postcure was done at 250°C for 1 h only, since stagewise heating at lower temperatures (refer to the Experimental section) already advanced the reaction.

Mechanical Properties of Laminate Composites

The mechanical properties of the laminates were examined as a function of composition of the blend and the nature of reinforcement. The resin content of 25–30% (by weight) was maintained. The trend in ILSS values given in Table II indicates that the resin/reinforcement interaction at the interface is not much affected by the composition of the matrix. However, in comparison to cured PMF, its blend with the PAF resin results in improved flexural strength of the composites, implying a comparatively reduced brittleness for the cocured matrix. This is reflected also in the

improved compressive strength of the blend, which increases directly with the allyl content of the blend. The trend in these values shows that allylphenol contributes to the enhanced ductility for the system since more allylphenol increases the chances of a linear structure in the network. Good mechanical performance is obtained for the blend with a composition corresponding to the optimum allylphenol:maleimide molar ratio 1:3. Compositions richer in PMF are more brittle and those with more allylphenol are more flexible. It may be noted that the properties obtained here are also superior to those of a conventional resole/silica laminate system.²⁵

Effect of Reinforcement

To study the effect of reinforcement on the mechanical properties of the composites, the reinforcement was changed to glass in a few cases. The mechanical properties of the resulting composites are compared with those of silica-reinforced composites in Table III. It is found that the resins show better wetting with glass reinforcement than with silica. The improved interaction between the resin and the reinforcement is evident from the increase in the ILSS values of the composites with glass fabric as the reinforcement. But the gain in ILSS was not translated to the flexural properties. The invariant or rather low flexural strength value suggests that failure occurs in the matrix under this shear mode. It has been reported that when the interphase is stronger failure of the composite could occur by fiber pullout or by matrix rupture.²⁶ The SEM photographs of the composite surfaces for two magnifications are given in Figures 6(A,B) and 7(A,B) for the silica and glass composites. The figures show a good adhesion of the resin to the fiber surface for

Table II Mechanical Properties of Silica Laminate Composites

Blend	ILSS (MPa)	Flexural Strength (MPa)	Compressive Strength (MPa)
MAP1	23.5 ± 1	203 ± 10	253 ± 15
MAP2	25.0 ± 1	209 ± 10	222 ± 10
MAP3	23.0 ± 1	202 ± 10	210 ± 10
MAP4	29.0 ± 1.5	204 ± 10	251 ± 10
MAP5	23.5 ± 1	176 ± 10	192 ± 20
PMF	24.0 ± 1	168 ± 10	157 ± 10
PMAF	20.0 ± 1	165 ± 10	171 ± 15

Table III Effect of Reinforcement on Mechanical Properties Laminate Composites

Resin	ILSS (MPa)		Compressive Strength (MPa)		Flexural Strength (MPa)	
	Silica	Glass	Silica	Glass	Silica	Glass
PMF 29	24 ± 1	34 ± 2	160 ± 10	290 ± 15	170 ± 10	190 ± 10
MAP 3	23 ± 1	36 ± 2	210 ± 15	293 ± 20	202 ± 15	180 ± 10
MAP 1	23.5 ± 1	44 ± 2.5	253 ± 15	300 ± 20	203 ± 15	163 ± 10

all cases. Fiber pullout is not seen but debonding is noticed to a negligible proportion, implying that the failure is mostly in the matrix. This is the reason for the nontranslation of the improved ILSS to the flexural properties on changing the reinforcement from silica to glass.

One-component Self-reacting Phenolic Resin (PMAF Resin)

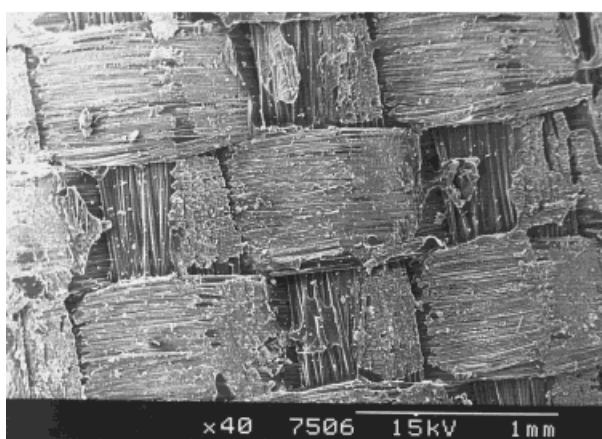
The extent of the cure and efficiency of the reactive blending depend, among many factors, on the accessibility of the reactive sites in the polymer chain and the miscibility of the components of the blends. Blends of polymers with a dissimilar backbone structure could face problems of immiscibility and consequent phase separation, leading to difficulty in the accessibility of the reactive functional groups located on them. This can be obviated if a single-component thermoset is employed. Thus, in one experiment, a phenolic resin containing both maleimidophenol (HPM) and allylphenol was synthesized by copolymerizing phenol, HPM, and allylphenol with formaldehyde. The synthesis is shown in Scheme 3. The resultant novolac contains HPM and allylphenol in the molar ratio 2:1 in the chain and is closer to the composition of the blend MAP 2 (refer to Table IV). The composition of the polymer was assessed from the N content and proton NMR. It contained 18.3 and 8.3% by weight of HPM and allylphenol groups, respectively. The signals due to =CH— appeared at 6 ppm (broad) and those due to =CH₂ at 5–5.1 ppm in ¹H-NMR, shown in Figure 8. The polymer characteristics are included in the Table I. The FTIR spectrum of the PMAF resin indicated the incorporation of both maleimide and allyl groups in the polymer chain. The C=O of the maleimide group and the C=C of the allyl group appeared at 1700 and 913 cm⁻¹, respectively, in addition to other characteristic absorptions. The FTIR spectrum is shown in Figure 3 along with other spectra.

The DSC cure profile of the PMAF resin manifested the three-stage curing similar to the MAP blend. The initial steps are more or less similar to those of the two-component systems. The DSC curve showed broad cure exotherms starting at 110°C. Unlike the blend, the high-temperature exotherm corresponding to the Diels–Alder reaction or the homopolymerization reaction extended from 225 to 350°C. The resin was cured under conditions identical to those for the two-component system. The mechanical properties of the composites of PMAF were found to be inferior to those of the two-component system of similar composition. It appears that the one-component polymer is comparatively more crosslinked and its brittleness attains that of the PMF resins. Enhanced crosslinking is a result of the better reactivity due to facile accessibility of the functional groups in the one-component polymer.

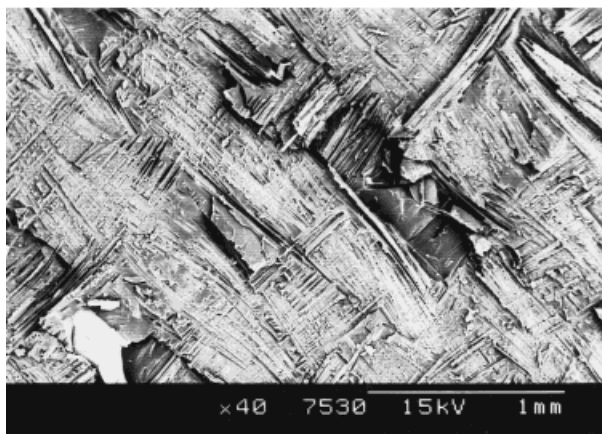
The PMAF resin was also evaluated as a matrix resin in laminate composites with silica as a reinforcement. The mechanical properties of the composite are included in Table II. The PMAF resin system exhibited ILSS values inferior and flexural strength values very close to those of the PMF resin. This system possesses both properties inferior to those of the two-component polymers of similar composition. This may also be a consequence of higher crosslinking, which is detrimental to the mechanical properties, as it would lead to brittle failure of the matrix in the composites. It appears that the composite fails in a brittle fashion in the matrix and not at the interphase. The SEM analysis of the fractured surface conveyed this information. The SEM photographs are shown in Figures 6(C) and 7(C) at two magnifications. The fiber wetting appeared to be excellent and even better than that of the two-component resin systems. Fiber debonding was practically not detected. This should have resulted in a stronger interface and higher ILSS. But the



A



B



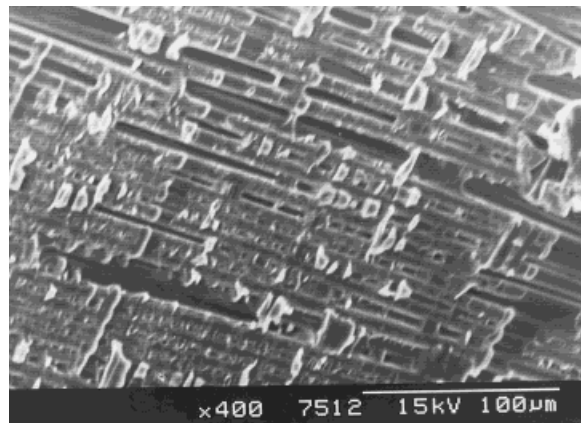
C

Figure 6 SEM photographs of fracture surface of composites with magnification $\times 40$: (A) MAP3 (silica); (B) MAP (glass); (C) PMAF-silica.

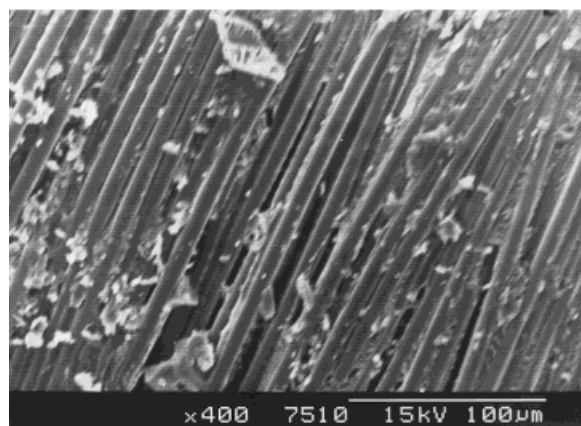
decrease in ILSS and flexural strength despite the good fiber wetting indirectly implied failure in the matrix.

Glass Transition Behavior of Composites

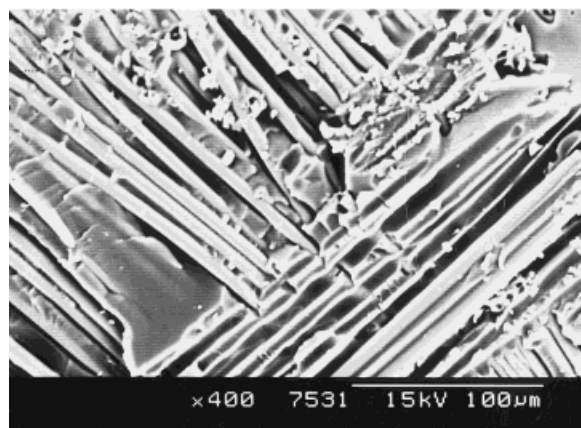
DMA of the cured blends showed only a single transition, indicating the existence of a single



A

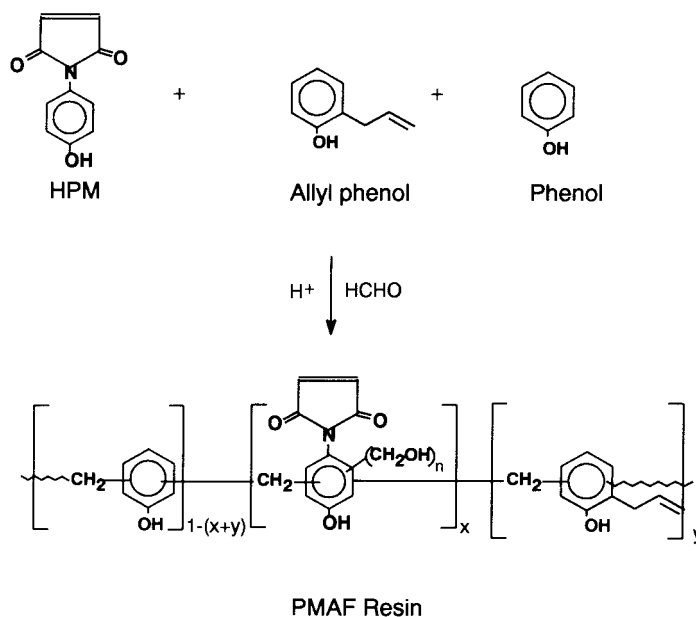


B



C

Figure 7 SEM photographs of fracture surface of composites with magnification $\times 400$: (A) MAP3 (silica); (B) MAP (glass); (C) PMAF-silica.



Scheme 3 Synthesis of PMAF resin.

phase. The T_g of the cured blends showed a marginal increase (170–178°C) with increase in the maleimide content. The DMA of a cured blend along with that of the PMAF resin is shown in Figure 9. The PMAF resin also exhibited a single transition (T_g) at 189°C. This resin possesses a marginally higher T_g compared to the blends, further confirming the higher crosslinking in this one-component system. The comparatively inferior T_g of the reactive blends, in general, could limit the prospects for high-temperature applica-

tion of the blends and their composites. DMA analyses showed the presence of a minor relaxation peak (from $\tan \delta$) around 275°C in both cases (Fig. 9). This may be caused by stress relaxation of the cyclic entities in the network, the exact origin of which remains to be investigated.

Thermal Characterization of Cured Blends

TGA of the cured blends shows mainly a two-step mass-loss pattern. Prior to these two steps, a mi-

Table IV Thermal Characteristics of Cured Blends (Heating Rate 10°C/Min, N₂ Atmosphere)

Ref. of Polymer Blend	Wt % PMF	MP:AP Mol Ratio	Major Decomposition Steps						Char Residue at 700°C
			Step 1			Step 2			
			T_i (°C)	T_f (°C)	Mass Loss (%)	T_i (°C)	T_f (°C)	Mass Loss (%)	
PAF	0	0:1	340	650	55	—	—	—	45.0
MAP1	61	1:1.2	345	440	6.5	440	630	24.6	62.0
MAP2	76	2:1.2	350	470	12.5	470	635	16.6	62.2
MAP3	82.2	3:1.2	355	430	5.3	430	700	30.0	62.4
MAP4	86.2	4:1.2	353	450	9.1	450	640	22.1	63.2
MAP5	88.7	5:1.2	385	445	6.1	445	640	21.1	65.5
PMF	100	1:0	340	420	6.7	420	700	19.4	69.9
PMAF	69	2:1.2	380	485	9.6	485	700	21.2	69.1

T_i and T_f , initial and final decomposition temperatures, respectively.

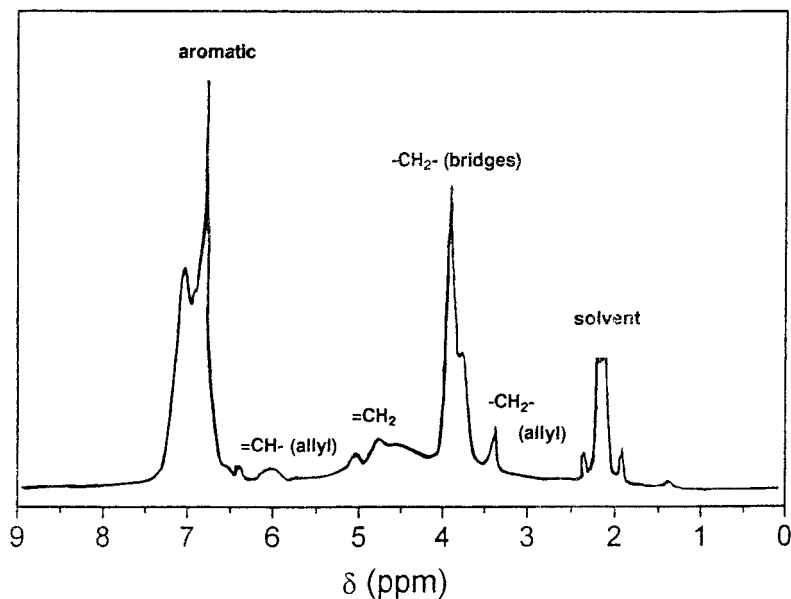


Figure 8 Proton NMR of PMAF resin in d_6 -acetone.

nor step occurs around 280–340°C for the blends and PMF resin. Mass loss at this temperature range is only 2–4%. The initial decomposition temperature of the blends is marginally superior to that of the cured component polymers and tends to increase with increase in the maleimide content. The anaerobic char yield was also enhanced with the maleimide content in a similar way. This is a consequence of the increased crosslinks through the formation of cyclic structures on increasing the maleimide content in the cocured system. Typical TGA curves of the cured

blend are shown in Figure 10. The thermal decomposition characteristics are given in Table IV.

The cured PMAF system exhibited better thermal stability than that of the two-component system of similar composition, that is, MAP 2. TGA showed single-step decomposition starting at 380°C, giving a char residue of 69% at 700°C for this system. The thermogram of PMAF resin is included in Figure 10.

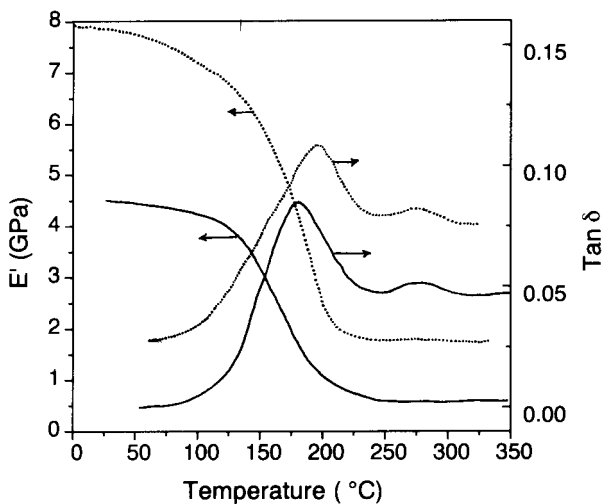


Figure 9 DMA spectra of (—) MAP2 and (---) PMAF at 1 Hz in nitrogen. Heating rate: 2°C/min.

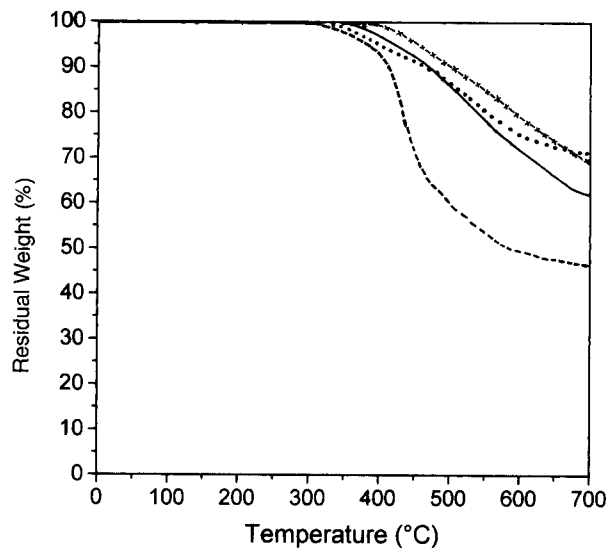


Figure 10 TGA of cured polymers in nitrogen: (· · · · ·) PMF; (---) PAF; (—) MAP3; (x-x-x-x) PMAF. Heating rate: 10°/min.

CONCLUSIONS

Reactive blending of maleimide- and allyl-functional novolacs results in a new addition-cure phenolic resin formulation. The systems cured through a sequence of reactions as evidenced from both DSC and DMA. Although the cure temperature remains independent of the composition, the isothermal gel time decreases proportional to the PMF content. The thermal stability of the cured network is superior to that of the component polymers and showed an increasing trend with increase in the maleimide content. Blending of PMF with PAF results in enhancement of the resin-dominant mechanical properties such as flexural strength and compressive strength of their laminate composites. Composite failure occurred in the matrix. Integrating the reactive components in a single polymer chain led to enhanced crosslinking, which resulted in better thermal stability but in poor or comparable mechanical performance of the composites derived from it. Changing the reinforcement from silica to glass brought about substantial improvement in the ILSS and compressive strength, but flexural strength remained unaffected or marginally reduced, implying matrix failure.

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