

Phenolic Resins with Phenyl Maleimide Functions: Thermal Characteristics and Laminate Composite Properties

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ABSTRACT: Phenolic resins bearing varying concentrations of phenyl maleimide functions were synthesized by copolymerizing phenol with *N*-(4-hydroxyphenyl)maleimide (HPM) and formaldehyde in the presence of an acid catalyst. The resins underwent a two-stage curing, through condensation of methylol groups and addition polymerization of maleimide groups. The cure characterization of the resin by dynamic mechanical analysis confirmed the two-stage cure and the dominance of maleimide polymerization over methylol condensation in the network buildup process. The kinetics of both cure reactions, studied by the Rogers method, substantiated the earlier proposed cure mechanism for each stage. Although the initial decomposition temperature of the cured resin was not significantly improved, enhancing the crosslink density through HPM improved thermal stability of the material in a higher temperature regime. The anaerobic char yield also increased proportional to the maleimide content. Isothermal pyrolysis and analysis of the char confirmed that pyrolysis occurs by loss of hydrocarbon and nitrogenous products. The resins serve as effective matrices in silica- and glass fabric-reinforced composites whose mechanical properties are optimum for moderately crosslinked resins, in which failure occurs through a combination of fiber debonding and resin fracture. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1664–1674, 2001

Key words: phenolic resin; addition cure; laminate composites; maleimide polymer; pyrolysis

INTRODUCTION

Despite possessing many attractive features such as thermal stability, solvent resistance, dimensional stability, and ablative property, the acceptance of phenolic resins as a universal material in many engineering areas is impeded by some of its inherent qualities, such as brittleness, poor thermo-oxidative stability, and the condensation nature of its cure reaction.^{1,2} A cure at high temperature by a condensation mechanism with evolution of volatiles, necessitates application of

pressure during molding to get void-free components, thus imposing processing restrictions. The need for use of a catalyst for curing and the limited shelf life of the resin at ambient conditions are also major shortcomings of these systems. In view of this, the need has been felt for the introduction of new cure chemistry, without evolution of volatiles and allowing for extended shelf stability at ambient conditions without impairing the thermal and thermomechanical characteristics. The concept of addition-curable phenolic resins gains significance in this context.^{3,4}

Tough, addition-curable, and thermally stable phenolic resins could answer many problems posed by conventional phenolics based on resole or novolac in terms of processibility and thermal

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and mechanical performance. Addition-curable phenolic resins with improved thermal and pyrolysis characteristics will be the desirable resins in composites for thermostructural applications.⁵ This is because the condensation cure leaves diffusion paths that allow for rapid absorption of moisture. The absorbed moisture, in addition to weakening the interfaces of the composite, paves the way for vaporization of the moisture during ablative heating, causing pressure buildup that again leads to interface weakening. A higher char yield also leads to better heat shielding. Such high-char phenolics could also be potential candidates as matrices in carbon-carbon composites, which would have obvious advantages.⁶

Addition-curable phenolic resins bearing allyl and vinyl groups have been reported.⁷⁻⁹ However, the thermally fragile crosslinks resulting in these cases adversely affect the thermal stability of the resulting phenolic resins. With a view to conferring addition cure property and thermal stability, we synthesized a series of phenolic resins bearing groups such as phenyl maleimide, propargyl ether, acetylene, and phenyl ethynyl groups.¹⁰ In a previous article we reported the synthesis and characterization of phenyl maleimide-functional phenolic resin by the reaction of HPM and phenol with formaldehyde.¹¹ Interestingly, the resulting resin was found to possess a very small concentration of methylol groups on a phenyl maleimide moiety, which conferred a partial condensation character to the resin. Whereas the previous article was concerned with the reaction mechanism and process optimization, the objective of the present work is to evaluate their usefulness as matrices in laminate composites for possible structural applications. This also necessitated a detailed investigation of cure characteristics and optimization of the cure process, which forms another objective of this study. To judge their potentiality in applications needing thermal resistance, understanding the thermal/pyrolysis behavior and char-yielding properties of these nonconventional resins becomes imperative. This article focuses on some of these aspects of the synthesized polymers.

EXPERIMENTAL

Materials

All solvents were of reagent grade. Resole was obtained from Propellant Fuel Complex, VSSC. It

was prepared under alkaline conditions with a phenol:formaldehyde ratio of 1:1. Silane-treated, plain-weave E-glass, 0.175 mm thick (Unnathi Corporation, Ahmedabad, India), and 8-harness satin-weave silica cloth (Valette High Temperature, Chennai, India), 0.5 mm thick, were used as reinforcements.

Instruments

FTIR spectra were recorded with a Nicolet 510P instrument. The cure characteristics of the resins were studied by differential scanning calorimetry (DSC) using a Mettler DSC-20 analyzer at a heating rate of 10°C/min over a temperature range of 30–350°C in a nitrogen atmosphere. Thermogravimetric analysis (TGA) 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 from room temperature to 700°C. Dynamic mechanical analyses were carried out on a DuPont DMA 983 with a DuPont 9900 thermal analyzer in a nitrogen atmosphere. Elemental analyses were obtained from a PerkinElmer model 2400 elemental analyzer. X-ray diffraction (XRD) analysis was carried out on a Philips X-ray diffraction unit with a PW 1729 X-ray generator having a vertical goniometer with a PW 1710 computer unit. Cu K α radiation was used with an accelerating voltage of 30 kV and a tube current of 20 mA.

Preparation of Composites

Silica-glass cloth was impregnated with a solution of the PMF resin in methyl ethyl ketone (MEK) and dried at room temperature for about 18 h. It was cut into 12 cm \times 10 cm pieces and stacked and molded in a hydraulic press between thick metallic platens to achieve the proper number of plies and thickness. The stack was initially heated at 100°C for about 45 min until the resin flow ceased and then progressively heated from 100°C to 250°C according to the following schedule:

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

A pressure of 200 psi was maintained throughout the temperature regime. A dried laminate prepreg ply was used for cure characterization by dynamic mechanical analysis (DMA).

Table I Characteristics of Purified PMF Resins

Polymer Reference	Weight (%) of HPM	Molecular Weight (GPC)				
		M_n	M_w	M_p	M_w/M_n	DP_n
PMF-19	19	1170	5800	3570	5.0	10.0
PMF-23	23	1140	5690	3270	6.7	9.6
PMF-29	29	1110	5860	2520	5.2	9.0
PMF-35	35	1040	6510	2440	6.2	8.2

Composite Testing

The mechanical testing of the composites was performed as per the following ASTM procedures using an Instron UTM model 4202.

Interlaminar shear strength (ILSS): ASTM D-2344-76 (volume 36, 1982).

Flexural strength: ASTM D-790-81 (volume 35, 1982).

0° Compressive strength: ASTM D-3410-75 (volume 35, 1982).

Resin-Content Determination

The resin content was determined by pyrolysis of specimens in air at 800°C for 4 h and by estimating the mass loss. The resin content was in the range of 26–30% by weight.

Thermal Curing

The thermal polymerization of the neat resins was effected by heating them in a vacuum oven slowly from room temperature to 250°C and maintaining this temperature for 2 h.

Pyrolysis

The cured resins were pyrolyzed in an Ar atmosphere (10 psi of excess pressure) in a furnace. A weighed quantity of samples was taken in preheated alumina crucibles, heated, and cooled, and the mass loss was noted.

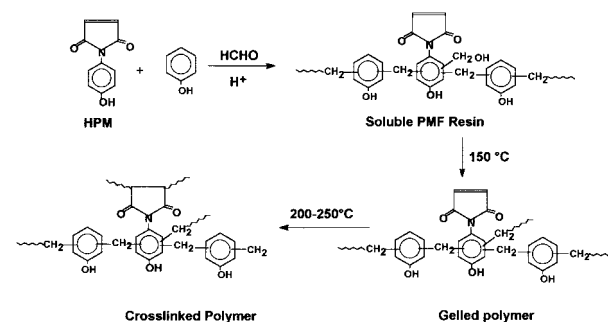
RESULTS AND DISCUSSION

Phenol-HPM-formaldehyde (PMF) resins with varying concentration of HPM were synthesized by copolymerizing the three components in the presence of oxalic acid catalyst as described previously.¹¹ Under the reaction conditions employed, a maximum of only 35 wt % of HPM could

be incorporated into the resin. Polymers with four different compositions and molecular weights, as given in Table I, were synthesized and were used for further studies. The structure of the polymer, established in the previous study, is shown in Scheme 1. The resin possesses a negligible concentration of methylol groups (4–6% by weight), which are on the phenyl ring of the HPM in the copolymer.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) analysis of PMF resins exhibited two exotherms regardless of the composition, indicating a two-stage curing. The DSC thermograms are shown in Figure 1. The exotherm in the low-temperature regime was attributed to both the methylol condensation and the assigning of around 250–300°C to maleimide polymerization. The temperature range of the first exotherm in DSC also corresponds to the condensation range of methylol groups in phenolic resole resins.¹² The DSC thermogram of a typical resole is included in Figure 1. Thus, it can be concluded that this exotherm is a result of the condensation of the methylol groups formed on the phenyl ring of HPM. Using TGA analysis, the methylol group concentration was estimated to be roughly 4–6% by weight of the uncured resin.¹¹

**Scheme 1**

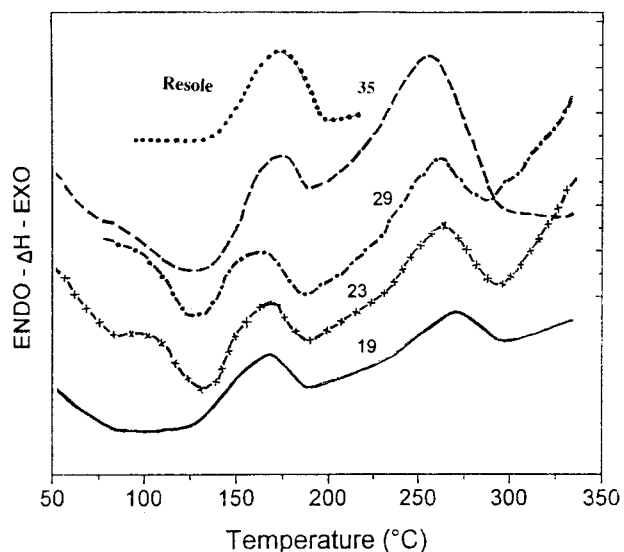


Figure 1 DSC thermograms of various PMF resins and Resole in N_2 . Heating rate of $10^\circ\text{C}/\text{min}$.

The second exotherm (with a peak at around 275°C) in the DSC of the PMF resin is typical of maleimide polymerization.^{13,14} The cure characteristics of the polymers are compiled in Table II. From the trend in temperature of cure onset (T_i) values, it can be seen that imide polymerization is facilitated as the polymer is enriched in it.

The glass-transition temperature of the copolymer, determined from DSC, did not show much dependence on maleimide content and was in the range of $120\text{--}130^\circ\text{C}$, which is marginally higher than the T_g of conventional novolac. On heating the resin, it softened at around the T_g , developed tackiness, and gelled at around 150°C . The complete curing occurred on heating it at 250°C .

Cure Kinetics

The activation energies (E) of the two curing steps were determined from DSC by the Rogers meth-

od,¹⁵ which is based on the hypothesis that the height of the exotherm (h_T) obtained in the DSC curve at any temperature is proportional to the rate of the reaction at that temperature.

$$h_T = C'(dH/dT)_T = C.k_T.(1-\alpha)^n \\ = C.A.e^{-E/RT}(1-\alpha)^n$$

n = order of reaction; α = fractional conversion at temperature T and C' are constants.

$$\ln(h) = \ln(C.A) + n \ln(1-\alpha) - E/RT$$

For small conversion intervals, the factor $\ln(AC) + n \ln(1-\alpha)$ can be considered practically constant because $\alpha \ln(1-\alpha) \ll \ln(AC)$. In other words, $[\ln(1-\alpha)^n + \ln(AC)] = C''$ is considered practically invariant over a small temperature range. Thus, the plot of $\ln(h_T)$ versus $1/T$ produces a straight slope equal to $-E/R$ and an intercept equal to C'' .

A typical plot for methylol group polymerization is shown in Figure 2, for PMF-29. Similar linear plots were obtained for both cure steps for all compounds. The collinearity of the experimental points supports the validity of the assumptions made. Activation energy (E) for both steps of all four compounds are given in Table II. The E values for the first exotherm show a general increase with an increase in HPM content, while for the second exotherm these values do not show any systematic trend. As discussed earlier, the first exotherm corresponds to the condensation of methylol groups, whose concentration increases with an increase in HPM content in the polymer. Thus, there is an increase in activation energy with an increase in the concentration of HPM and the methylol content in the PMF resin. It can be noted that the calculation of activation energy

Table II DSC Cure Characteristics of PMF Resins Heating Rate $10^\circ\text{C}/\text{min}$

Polymer	First Exotherm				Second Exotherm			
	T_i ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_e ($^\circ\text{C}$)	E_1 (kcal/mol)	T_i ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_e ($^\circ\text{C}$)	E_2 (kcal/mol)
PMF-19	140	175	196	12.5	250	280	300	20
PMF-23	140	175	198	15.4	240	272	300	25
PMF-29	140	170	197	23.8	238	270	302	28
PMF-35	140	184	195	29.5	200	265	305	22
Resole	133	176	210	17.2	—	—	—	—

T_i = cure initiation, T_p = cure maximum, T_e = cure end temperature, E = activation energy.

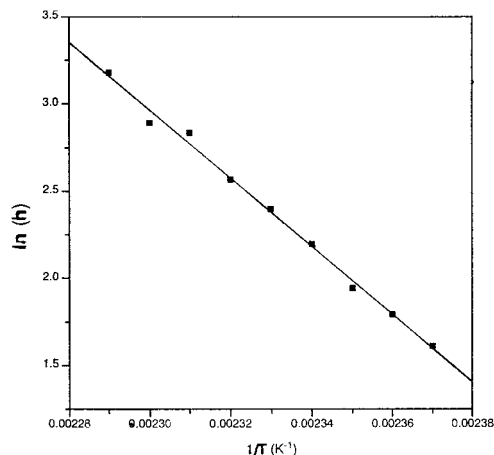


Figure 2 Rogers plot for determination of activation energy for the methylol condensation of PMF-29.

from the DSC exotherm is subject to error because of the associated endothermic process caused by volatilization of the condensate, such as water and formaldehyde. Hence, the values reported here cannot be considered absolute and are only given for comparison among the polymers. The cure kinetics could not be followed by more accurate techniques such as FTIR because of the poor sensitivity of the weak absorption bands corresponding to the methylol groups, present only in minor quantities in the polymer.

For a comparison, E for conventional resole was also estimated by the same method, and its value was to fall in the same range as that for PMF resins having comparatively less HPM content. This lends support to the hypothesis that the first exotherm could be the result of the methylol condensation reaction in PMF. Further, it may be concluded that the condensation of methylol groups (in PMF) with a phenol moiety is disfavored by the proximity of the less reactive HPM, as the concentration of the latter increases in the chain. The steric hindrance offered to methylol condensation by the HPM moiety might also be responsible for the apparent increase in activation energy with an increase in HPM content of the PMF resin. The activation energy calculated for the maleimide polymerization is in the same range as that for the thermal polymerization of HPM reported in a separate study ($E = 21$ kcal/mol).¹⁶ Estimation of this parameter by the Rogers method might not be associated with error, as this step corresponds to an addition reaction. The activation parameters are helpful for predicting the cure profile of the resins under a given set of conditions.

Thermal Curing

The PMF resins were cured by heating them in an oven from room temperature to 250°C and maintaining them at this temperature for 2 h under vacuum. The cured polymer was completely insoluble in common organic solvents. The FTIR spectra of the cured resins were not much different from those of the prepolymers, as the characteristic absorptions due to unsaturation of the prepolymer merged with other peaks and its disappearance on curing could not be differentiated. The variation in intensity of the characteristic absorption of the =C—H group of maleimides appearing at 690 cm⁻¹ was too insensitive to serve as a probe for cure monitoring. The only notable change was a decrease in the relative intensity of the C=O absorption at 1720 cm⁻¹, which is usually observed when maleimide is transformed to succinimide on polymerization.¹⁷ The FTIR of the cured polymer are shown with that of its precursor in Figure 3. The completion

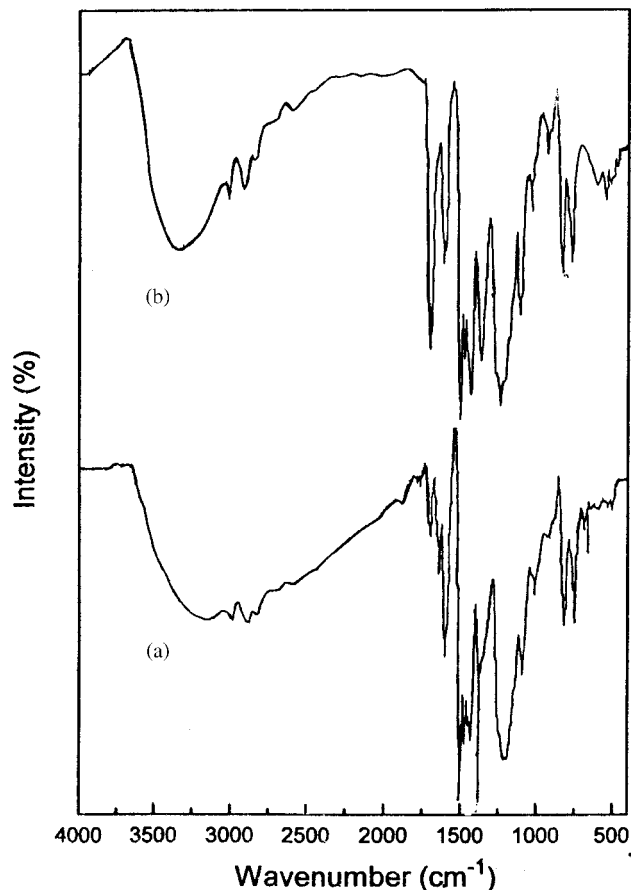


Figure 3 FTIR (KBr) spectra of PMF-35: (a) cured and (b) uncured resin.

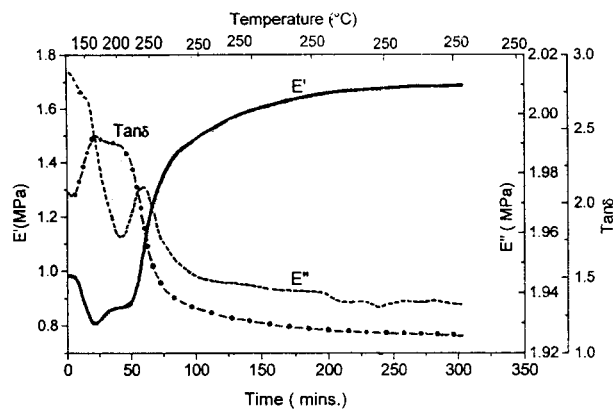


Figure 4 Dynamic mechanical analysis of single-ply prepreg of PMF-29. Heating rate for dynamic part: 2°C/min. Isothermal heating at 250°C. 1 Hz. Nitrogen atmosphere.

of curing was confirmed from the isothermal DMA of the prepreg of PMF done at 250°C, to be discussed later. The thermal stability of the cured resins was examined by TGA.

Evaluation as Matrix in Laminate Composites

Cure Optimization

The PMF resins were evaluated as matrix resins in composites with silica and glass-fabric reinforcements. The prepregging was done by a solution-dipping process. On heating the prepreg, the polymer softened initially and developed tackiness. At around 150°C the system gelled partially through condensation of methylol groups, and the resin flow ceased. On heating further, to 250°C, polymerization of the maleimide took place, and the polymer became rigid. The cure schedule for molding the composites was optimized from the DMA analysis of the single-ply prepreg. The mixed mode (dynamic and isothermal) DMA curves of PMF-29 and PMF-35 at two different temperatures are shown in Figures 4 and 5, respectively. The DMA curves manifest the same two-stage curing as seen in the DSC at more or less the same temperature range. However, the increase in storage modulus (E') because of the methylol condensation works out to be negligibly small when compared to that because of the maleimide curing. This implies that the concentration of these condensable groups is negligible and that the major crosslinking proceeds via imide polymerization. DSC does not give this differentiation because maleimides generally have a low

heat of polymerization and do not show a strong exotherm, in contrast to the methylol condensation associated with a high heat of reaction. Consequently, the latter reaction gives rise to a disproportionately strong exotherm in DSC. The DMA, at a heating rate of 2°C/min, shows that the gelation occurs at around 150°C, where the E' and E'' cross (Fig. 4). The DMA, run till 250°C under dynamic conditions followed by isothermal heating at this temperature for 3 h, shows that at 250°C the postcuring is found to proceed for about 2 h, when E' becomes almost stagnant. The curing was almost 90% complete on keeping it at 250°C for 1 h, after which the buildup in the property (E') was very slow. Isothermal DMA for PMF at 300°C shows that the postcuring continues at this temperature for about 90 min and that the additional buildup in property is not significant at this temperature.

Since the cure temperature of 300°C is undesirable and can lead to minor degradation, the final cure temperature was restricted to 250°C and the postcuring time to 1 h at this temperature. An earlier polymerization study had revealed that HPM can be completely cured under isothermal conditions at 250°C.¹⁶ The cure schedule given for the fabrication of composite is given in the experimental section. The compaction of the laminates was done after partial isothermal gelation of the resin at 100°C, when gelation occurs through the condensation of the methylol groups. Postcuring was done at 250°C for 1 h. In some cases in order to study the effect of cure temperature on composite properties, the final curing also was done at 200°C. Partial curing at a

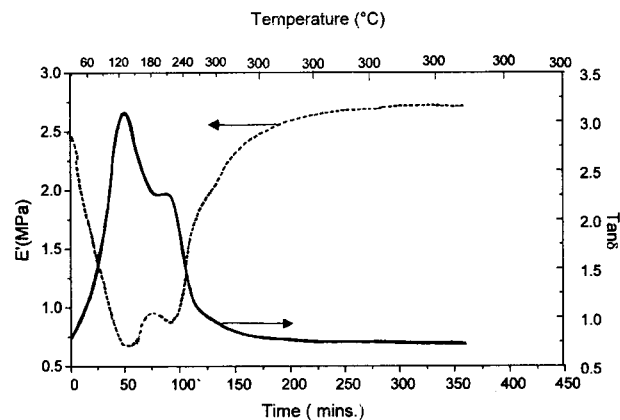


Figure 5 Dynamic mechanical analysis of single ply prepreg of PMF-35. Heating rate for dynamic part: 2°C/min; isothermal heating at 300°C.; 1 Hz; nitrogen atmosphere.

Table III Mechanical Properties of Laminate Composites Using Silica Reinforcement—Effect of Composition and Cure Temperature

Resin	ILSS (kg/cm ²)		0° Compr. Str. (kg/cm ²)		Flex. Str. (kg/cm ²)		Resin Content (wt %)
	200°C	250°C	200°C	250°C	200°C	250°C	
PMF-19	110	170	390	1040	840	1780	30
PMF-23	160	230	740	2020	1470	1900	30
PMF-29	180	240	550	1600	1660	1700	30
PMF-35	—	220	—	1500	—	2000	31
PMF-29 ^a	—	340	—	2900	—	1900	30
Resole	—	190	—	1500	—	—	—

^a Reinforcement, E-glass.

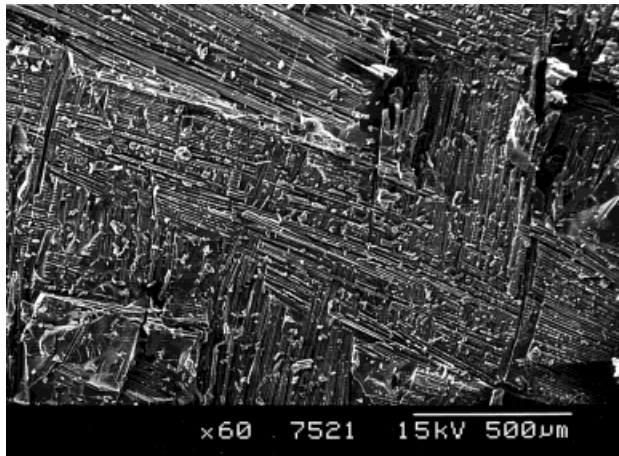
lower temperature is the coup de grâce for molding PMF resin because this reaction precludes the bleeding of the resin at a higher temperature, normally needed for crosslinking the system through the maleimide group.

Mechanical Properties of Composites

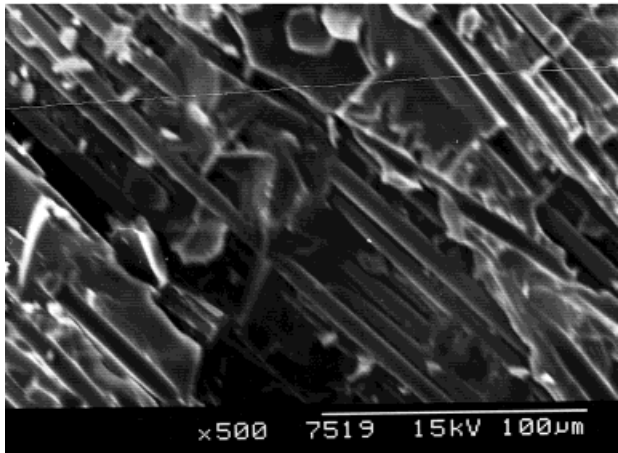
Phenolic composites are generally not recommended for structural applications but are excellent for thermostructural purposes.¹ To evaluate the usefulness of this new resin as matrices in composites, the mechanical properties of the laminates were examined as a function of polymer composition and cure temperature. The properties are compiled in Table III. When cured at 200°C, the mechanical properties, particularly ILSS and flexural strength, tend to increase as the maleimide concentration in the resin increases. This could be attributed to the increased crosslinking as the polymer gets enriched in the maleimide group. At this cure condition the resin is only partly cured. The extent of cure, estimated based on studies on the model compound (done by thermally polymerizing HPM under identical conditions and estimating the polymer content by GPC¹⁶), worked out to be about 78%.

As the cure temperature is increased to 250°C for 1 h, nearly all maleimide groups are polymerized (as confirmed from the study of the model compound, HPM¹⁶), and it is reflected in the improved mechanical properties of the composites. It was found that on curing at 250°C, the mechanical properties of the composites show an initial increase with an increase in maleimide content (and consequently the crosslink density). However, at still higher degree of crosslinking, the embrittlement effect causes easy fracture (lower

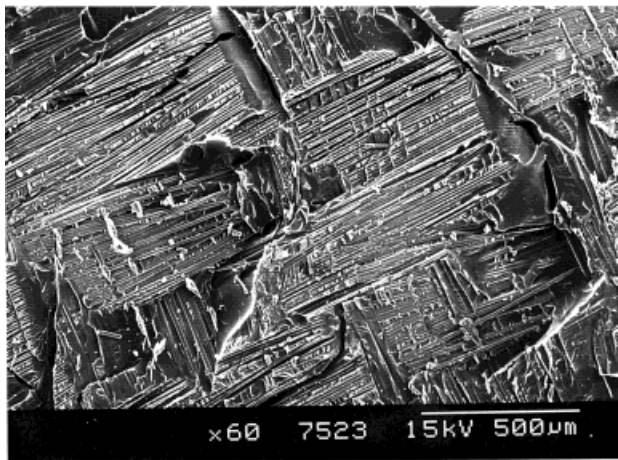
compressive strength). ILSS apparently decreases because the composite could fail, apart from fiber debonding, also through the brittle fracture of the matrix, as seen in SEM photographs of the fractured surface, shown in Figure 6(a,b). The best properties were obtained for the resin containing 29 wt % of maleimide (PMF-29). Thus, for the HPM-rich systems (e.g., PMF-35), better properties are achieved for incomplete cure of the maleimide functions. This provides additional justification for a postcure time of 60 min at 250°C, although DMA suggested 120 min. It may be noted that the cure characterization through DMA indicates a buildup of the rigidity of the system, and it does not reflect the interlaminar or compressive properties of the composites, which have to be optimized through actual experimentation, as was done here. It may also be noted that the mechanical properties of the PMF-based composites are better than those reported for a resole-based system,¹⁸ though a strict comparison between the two is not justified, as the latter system is cured by a different mechanism with a different cure schedule. The mechanical properties of composites of PMF were found to improve on changing the reinforcement to glass because of better fiber wetting, resulting in a stronger interphase. This was again evident from the SEM photographs of the fractured surface of the glass composite, shown in Figure 6(c), which shows good fiber wetting. Virtually no debonding is seen, unlike with silica reinforcement. In some pictures matrix failure is clearly seen. In the case of glass reinforcement, failure is observed in the matrix and not at the interphase. It is known that in the case of a strong interphase, the bulk property of the resin limits the mechanical properties of the composites. But for the processing restric-



(a)



(b)



(c)

Figure 6 SEM photographs of fractured surface of laminate composite of PMF-29: (a) silica, magnification 60; (b) silica, magnification 500; (c) glass, magnification 60.

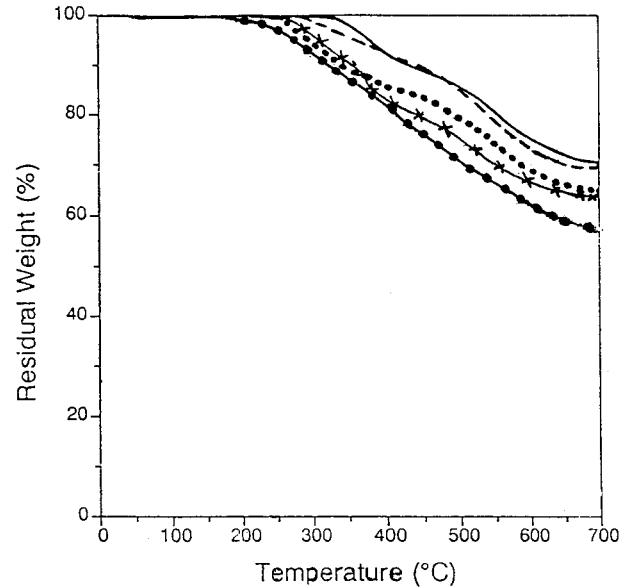


Figure 7 Thermograms of cured phenolic resins: (—x—x—) PMF-19; (•••••) PMF-23; (— — —) PMF-29; (——) PMF-35; (•••••) resole in nitrogen. Heating rate 10°C/min.

tions imposed by the high-temperature cure, the systems are found to be useful for composites with moderate strength requirements.

Thermogravimetric Analyses

In order to assess the suitability of the resin for thermostructural composite applications, it is imperative to know its thermal behavior. The PMF resins required for TGA analysis were obtained by heating them in a vacuum oven at 250°C for 2 h. The thermal stability of the cured resins was examined by thermogravimetric analysis (TGA). The thermograms of the polymers of different compositions are shown in Figure 7. Although the initial decomposition temperature is not significantly improved in comparison to cured resole, enhancing the crosslink density through HPM resulted in increased thermal stability of the material in a higher temperature regime. The low initial decomposition character is a result of considerably less crosslinking in contrast to resole. Despite the poorer crosslinking, relatively improved T_i values (vis-à-vis resole) attests to the thermal stabilization effect of maleimide in the phenolic resin. The anaerobic char yield increased proportional to the maleimide content. It can be seen that about 70% char yield was obtained at 700°C for PMF-29 and PMF-35, in contrast to conventional phenolic resins, which produce only

Table IV Pyrolysis Results on PMF-29 and Resole Resins

Polymer	% Age of Functionalization	Mass Loss During Curing (%)	Char at 700°C (from TGA) (%)	Char Remaining after Pyrolysis at 700°C (%)		Char Remaining after 2 h at 900°C (%)
				1 h	2 h	
PMF 29	29	6	70	62	60	60
Resole	49	22	61	60	59	59

around 60% char under the same conditions. The thermogram of cured resole is also included in Figure 7 for a comparison. The slow degradation rate and comparatively higher char residue of the resin with an increase in maleimide content imply a better potential for their use in thermostructural applications where a higher char-yielding property is advantageous.^{5,6} For the same reason these polymers have an edge over the conventional phenolics for use as matrices in carbon-carbon composites. In this context it should be noted that conventional resole resins used for carbon-carbon composites already lose about 22–28% mass during the initial curing process, in contrast to PMF resins, which lose only 4–6% volatiles during curing at 250°C. The absolute amount of char produced per unit of phenolic resin is therefore significantly higher for PMF resins as compared to resoles. The use of PMF in place of resole would therefore reduce the number of pyrolysis steps required for carbon-carbon composites, of course, subject to the good integrity of the char formed, which needs to be investigated separately.

Pyrolysis

Although TGA helps derive an overall assessment of the thermal stability and anaerobic char residue under dynamic heating mode, a true understanding of the carbonization process warrants isothermal pyrolysis and char analysis, which have been done for a selected PMF polymer in a limited temperature regime. The pyrolysis data could be useful information for judging its potential applications as ablative materials and as matrices for the preparation of carbon-carbon composites. Pyrolysis was done at 700°C and 900°C, and the char yield and the nature of the char were analyzed. The isothermal pyrolysis at temperature 700–900°C was effected in an inert atmo-

sphere of argon for different time intervals. The char obtained after pyrolysis was gravimetrically estimated and analyzed for composition.

The percentages of char remaining at 700°C and at 900°C after 1 and 2 h of pyrolysis of PMF and resole are compiled in Table IV. The pyrolysis data show that the char is nearly stabilized at 700°C. Although TGA showed appreciable differences, the char residue under isothermal pyrolysis of the cured PMF resin was comparable to that of cured resole. This difference arises from the difference in the kinetics of degradation of the two compounds, especially under the dynamic heating conditions in TGA. The char was analyzed for elemental composition and also by IR and XRD.

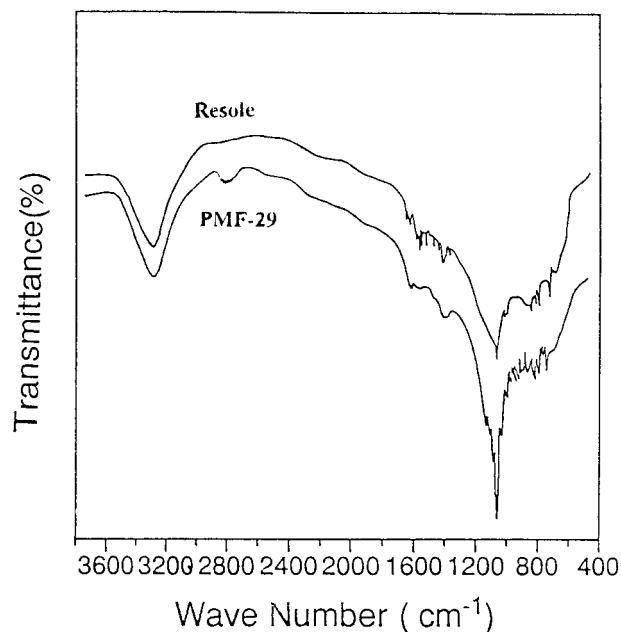


Figure 8 FTIR (KBr) of the pyrolyzed residues of PMF-29 and resole.

Table V Composition of Char Formed after Pyrolysis at 700°C for PMF-29

Pyrolysis Conditions	Char (wt %)	C (%)	H (%)	N (%)	O (%) ^a
Virgin resin	—	74.6	5.1	2.0	18.3
700/1 h	62	79.9	1.4	1.0	17.7
700/2 h	62	80.0	1.2	0.9	17.9
900/2 h	60	83.9	1.4	0	14.7

^a Indirectly estimated from the difference.

FTIR Spectral Analysis of Char

FTIR of the pyrolyzed samples shows weak broad absorption at 1000–1200 cm⁻¹. This may be because of the residual C—O linkages present in the system. Under the limited pyrolysis temperature conditions, it might not be possible to eliminate the oxygen atom completely. Very minor absorption, corresponding to C—H groups, was seen at 2900–2980 cm⁻¹. C—OH absorptions were observed at 3300–3600 cm⁻¹. Both spectra resemble that of commercial charcoal. The FTIR spectrum of pyrolysates of resole and PMF (after pyrolysis at 900°C for 2 h) are shown in Figure 8.

Elemental Composition

The percentages of C, H, and N in the residue obtained after pyrolysis at 700°C and 900°C are given in Table V. On increasing the pyrolysis time at 700°C, the percentage change in elemental composition was negligible. On heating to 700°C, the elemental composition change for nitrogen and hydrogen only. During this stage degradation may be occurring via loss of hydrocarbons and possibly of nitrogenous derivatives. On increasing the temperature to 900°C, both nitrogen and oxygen decreased, possibly through loss of oxides of nitrogen, indirectly enhancing the carbon content. The char possesses a significant amount of oxygen (which was estimated indirectly and confirmed from IR). Complete pyrolysis needs a still higher temperature, which remains to be studied. XRD analyses of the char revealed them to be amorphous in nature.

CONCLUSIONS

New addition-cure phenolic resins (PMF) containing varying proportions of maleimide functions could be synthesized by copolymerizing phenol

and *N*-(4-hydroxyphenyl) maleimide with formaldehyde in an acidic medium. The cure characteristics of the resins were studied by DSC, which showed two-stage curing. At a lower temperature the resin gels through the condensation reaction of the residual —CH₂OH groups formed on the maleimide moiety. This confers a partial condensation character to the resin. Major curing occurs through the addition polymerization of maleimide at 250°C. The two-stage curing was further confirmed by DMA analysis of the prepreg of the resin. The mechanical properties of the silica laminate composites were better than those of conventional phenolics and were found to be dependent on the maleimide content and its extent of cure. A system with moderate crosslink density showed good mechanical properties for the composites whose failure occurred through a combination of fiber debonding and resin fracture. On enhancing the crosslink density further in systems with a higher maleimide content, failure of the brittle matrix was observed. Replacement of silica by glass reinforcement resulted in a stronger interphase, in which failure occurred mainly in the matrix. The resins were found to have an excellent shelf life at room temperature and are storable as fine powder. The partial condensation cure character at lower temperatures is conducive to preventing the melt flow of the resin at higher temperatures during molding and fabrication of composites.

REFERENCES

- Knop, A.; Pilato, L. A. *Phenolic Resins; Chemistry, Application and Performance, Future Directions*; Springer-Verlag: Heidelberg, 1985.
- Kopf, P. W.; Little, A. D.; In *Kirk-Othmer Encyclopaedia of Chemical Technology*; Wiley & Sons: New York, 1991; vol. 18, p 603; *Encyclopaedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F.,

- Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley & Sons: New York, 1988; Vol. 11, p 45.
3. Reghunadhan Nair, C. P.; Bindu, R. L.; Ninan, K. N. Recent Advances in Phenolic Resins, Metals, Materials and Processes; Radhakrishnan, G., Ed.; Meshap Publications: Mumbai, 1997; Vol. 9(2), p 17.
 4. Reghunadhan Nair, C. P. In Recent Developments in Phenolic Resins, Addition-Cure Phenolics; Proceedings of Polymers '99, International Symposium on Polymers Beyond AD 2000; Ghosh, A. K., Ed.; Society of Polymer Science: New Delhi, 1999; p 35.
 5. Katsman, H. A.; Mallon, J. J.; Barry, W. T.; *J Adv Mater* 1995, 4, 21.
 6. Golfarb, I. J.; Lee, C. Y.-C.; Arnold, F. E.; Helminiak, T. E. In High Temperature Polymer Matrix Composites; Serafini, T. M, Ed.; Noyes Data Corporation: Park Ridge, NJ, 1987; p 2.
 7. Hui, K. M.; Yip. L. C.; *J Polym Sci, Polym Chem* 1976, 14, 2323.
 8. Moroz, S. A.; Gorbachev, S. G.; Chekina, O. V. *Plast Massy* 1987, 8, 34.
 9. Tomatsu, Y.; Sumaya, M.; *Jpn Kokai Tokkyo Koho, JP 07, 150008; Chem Abstr* 1995, 123, 230290.
 10. Bindu, R. L. Ph.D. Thesis, Kerala University, India, 2000.
 11. Reghunadhan Nair, C. P.; Bindu, R. L.; Ninan, K. N.; *J Polym Sci Polym Chem Ed* 2000, 38, 641.
 12. King, W.; Mitchell, R. H.; Westwood, A. R., *J Appl Polym Sci* 1974, 18, 1117.
 13. Kenny, J. M.; Pisaniello, G.; Farana, F.; Puzziello, S.; *Thermochim Acta* 1995, 269/270, 201.
 14. Morgan, R. J.; Robert, J.; Douglas, L. E.; Edward, E. J. 22nd International SAMPE Technical Conference, Nov. 6-8, 1990, p 145.
 15. Rogers, R. N.; Morries, E. D.; *Anal Chem* 1992, 38, 412.
 16. Gouri, C.; Reghunadhan Nair, C. P.; Ramaswamy, R. *J Appl Polym Sci* 1999, 73, 95.
 17. Reghunadhan Nair, C. P.; Tania Francis *J Appl Polym Sci* 1999, 74, 3365.
 18. Usha, K. M.; Balakrishnan, T. R.; Alwan, S.; Sastri, K. S. *Macromolecules, Current Trends; Venketchalam, S.; Joseph, V. C.; Ramaswamy, R.; Krishnamurthy, U. N., Eds.; Allied Publishers: New Delhi, 1995; Vol. 1, p 42.*