

Diallyl Bisphenol A—Novolac Epoxy System Cocured with Bisphenol-A-Bismaleimide—Cure and Thermal Properties

K. Ambika Devi, C. P. Reghunadhan Nair, K. N. Ninan

Propellants, Polymers, Chemicals, and Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, India

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ABSTRACT: Novolac epoxy (EPN)—2,2'-diallyl bisphenol A (DABA) resin system was modified by cocuring it with bisphenol A bismaleimide (BMI). Molar concentration of BMI in the stoichiometric blend of EPN and DABA was varied from 0.5 to 2.0. The cure optimization was done using DSC, IR spectroscopy, and rheological studies. The curing proceeded by phenol-epoxy and Alder-ene reactions. The performance of the ternary Epoxy-Allyl phenolic-Bismaleimide system was evaluated through their thermal and dynamic mechanical characterization. BMI improved the overall thermal stability and the modulus of the result-

ant composites. The increase in BMI concentration in the system resulted in enhanced glass transition temperature with a consequent improvement in high temperature performance typically estimated by their lap shear strength at high temperatures. The high temperature performance of the epoxy-phenol-bismaleimide (EPB) system was found to be far superior to the epoxy-phenol (EP) system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1192–1200, 2007

Key words: epoxy-phenol-bismaleimide; modified epoxy; high performance matrix

INTRODUCTION

The process of selecting an epoxy matrix for structural application usually begins with the requirement of its T_g , stiffness, hot-wet property retention, and possibly its physical and chemical properties. While the physical and chemical properties which are material characteristics are governed by the chemical species in the molecule, the T_g and stiffness of the epoxy matrix strongly depend on the structural arrangement of molecules i.e., the rigidity of the molecular chain and its crosslink density. The two important drawbacks of the epoxy systems which restrict their use in advanced composites are their brittle nature and poor high temperature properties. Several studies have been carried out to improve the toughness^{1,2} and high temperature performance^{3,4} of epoxy matrix system. While matrix toughening using suitable materials is mostly resorted to for eliminating the brittleness of the system, improvement of its high temperature property is ensured mostly by the modification of resin itself, selection of suitable curing agent and/or by using binary and ternary polymer blends.⁵ The blending of two or more polymeric phases has been shown to be an effective way for deriving tailor-made matrices.

However, due to phase separation between the two components, the expected properties are always not attained. The interaction between the component phases may, however, be brought about by the addition of an agent that reacts with both the phases and render them mutually compatible.⁶ Such engineered systems can withstand the service temperatures and loads experienced by modern aerospace equipments.

Thermoset-thermoset blends have been formulated to balance between thermal and mechanical properties of the epoxy resin system.^{7–9} Vanaja and Rao¹⁰ carried out thermal studies on BMI blended epoxy-amine matrix systems and reported improved thermal stability for their composites. Park et al.¹¹ developed a new siloxane-containing curing agent from epoxy-terminated siloxane oligomer (ESTO) and diamino diphenyl methane (DDM) by hot-melt method and found that the thermal stability factors of the Epoxy-ESTO-DDM systems were enhanced with an increase in the ESTO content. Fluorine-based epoxy resins have been formulated to introduce the rigidity and to increase the heat resistance of the conventional epoxy resin, DGEBA. These resin systems cured with di (*p*-aminophenyl) sulfone have high glass transition temperature (>187°C) and excellent stiffness. Ortho-substitution provides cured epoxy systems with improved stiffness.¹² Shenoy and Patil¹³ modified the DDM-cured epoxy resin (DGEBA) by reacting it with different concentrations of bismaleimide in presence of unsaturated polyester

Correspondence to: C. P. R. Nair (cprnair@gmail.com).

and observed that the addition of BMI improved the mechanical performance.

In our earlier studies¹⁴ we have observed that a dual curing mix of novolac epoxy and 2,2'-diallyl bisphenol-A has resulted in an improved quality matrix resin with good composite properties. However, the utility of the system was again limited by its low T_g . The presence of allyl groups offered possibility for further matrix modification. Self-curing of allyl groups was conducive to marginal enhancement in properties and T_g . In this work, allyl groups in the epoxy-phenolic matrix was reacted with a bismaleimide to modify the matrix. The reaction between phenyl allyl and maleimide groups is well established.^{15,16} The reaction proceeds by a sequence of Ene reaction followed by Diels–Alder reaction, depending upon the cure temperature.¹⁷ The network structure depends also on the backbone structure and also on the stoichiometry of the allyl and maleimide groups.¹⁸ The present study effectively describes an attempt made to improve the T_g and hence the high temperature properties of the novolac epoxy–2,2'-diallyl bisphenol A system (EP) by its reactive blending with bisphenol A bismaleimide (BMIP). BMIP was chosen because of its similarity in backbone structure to the DABA curative. BMIP concentration in the ternary blend was varied and the system was evaluated for its rheological, dynamic mechanical, and the thermophysical characteristics. The synthesis and physicochemical characterization of the ternary reactive blend of novolac epoxy–diallyl bisphenol–bismaleimide have been scarcely addressed.

EXPERIMENTAL

Materials and methods

Materials

The source and structure of materials used for the study are given in Tables I and II.

TABLE I
The Constituents of EPB System and Their Sources

Diallyl bisphenol A (DABA)	Synthesized from bisphenol A and by a known procedure ¹⁹
Epoxy resin (EPN 1139)	Supplied by Ciba Geigy, Mumbai, India
Triphenyl phosphine (TPP)	Supplied by E-Merck, India and used as received
Bis (4 maleimido phenoxy) phenyl propane (BMIP)	Synthesized by a reported procedure ²⁰
E-glass cloth	Plain weave, silane treated E-glass fabric of thickness 0.25 mm from Unnathi Corporation, India

Preparation of ternary blend

Novolac epoxy (10 mequiv) and diallyl bisphenol A (10 mequiv) were weighed in a 100-mL reaction flask. Known weight of triphenyl phosphine (TPP) was added to this flask (0.5% of the total weight of the two components). Calculated amount of bisphenol A bismaleimide (typically 10 mequiv) was then added so that the equivalent ratio of the three components in the ternary blend is 1 : 1 : 1. The resin blend was prepared by dissolving it in sufficient quantity (~ 50 mL, ~ 10 times the weight of the polymer blend) of AR acetone, heating to 60°C for complete dissolution and evaporating the remaining acetone. Complete removal of solvent was achieved by heating it in a vacuum oven at 60°C. The same procedure was repeated by varying the equivalent concentration of BMIP from 0 to 2.0 in steps of 0.5.

Characterization of uncured ternary blend

Spectroscopic analysis

Fourier Transform infrared spectroscopy (FTIR) was employed for the cure characterization of the matrix system. Samples were scanned for characteristic functional group absorptions in a Perkin–Elmer Spectrum GX A FTIR spectrophotometer for a wave number range of 4000–400 cm^{-1} .

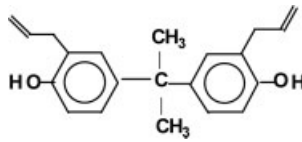
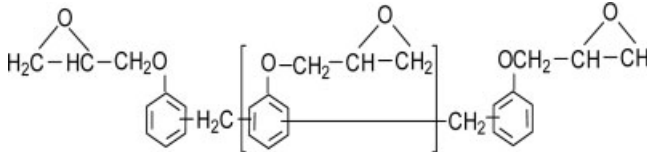
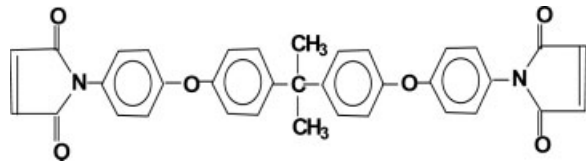
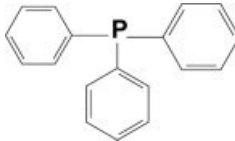
Thermal characterization

Differential scanning calorimetric (DSC) studies were carried out using a Mettler TA 3000 thermal analysis system in conjunction with TC-10A TA processor and standard DSC-20 analyzer using aluminum sample pans. The heating rate employed was 10°C/min from room temperature to 300°C in nitrogen atmosphere. Glass transition temperature (T_g), extent of cure reaction, temperatures at cure initiation (T_i), and completion (T_c) and peak reaction temperature (T_m), were noted from dynamic DSC thermograms.

Rheological characterization

The rheological analysis was done with a Reologica Stress Tech Rheometer. The instrument was used in the oscillation mode using a parallel plate assembly (20-mm diameter) with a gap of 0.5 mm in a controlled strain mode. The storage shear modulus G' , loss shear modulus G'' , and complex viscosity η^* were measured as a function of temperature. Isothermal rheological studies were also carried out by recording the above parameters as a function of time at the required temperatures.

TABLE II
Structures of Constituents of EPB System

Materials	Structure
Diallyl bisphenol (DABA)	
Novolac epoxy (EPN)	
Bis (4 maleimido phenoxy) phenyl propane (BMIP)	
Tri phenyl phosphine (TPP)	

Preparation of neat resin moldings

The EPB systems with different concentrations of bismaleimide were cured in a vacuum oven, following the optimized cure conditions given below. The cure conditions were fixed based on the DSC and rheological test results. The final curing was done by heating the same at 250°C for 5 h as per the time-temperature schedule given below.

Temperature	100	150	200	250
Hold time (min)	60	30	60	300

Characterization of cured ternary blend

Thermo gravimetric analysis

Nonisothermal thermo gravimetric analysis was performed on cured, neat samples in nitrogen atmosphere at a heating rate of 10°C/min from ambient to 700°C using a Du Pont 951 thermal analyzer. The initial decomposition temperature (TG_i), temperature of maximum thermal decomposition (TG_m), and the temperature of completion of thermal decomposition (TG_c) as well as the char-yield were obtained from the TGA thermograms.

Dynamic mechanical analysis

Isothermal and dynamic DMA studies were performed for the cure characterization and cure optimization of the matrix systems and to evaluate their visco-elastic properties. A Du Pont DMA 983 model instrument was used for the purpose. For analysis in the dynamic mode a heating rate of 5°C/min was used from room temperature to 300°C. Analyses were carried out in nitrogen atmosphere at a fixed frequency of 1 Hz and the flexure storage (E') and loss (E'') moduli as well as shear storage (G') and loss (G'') moduli and loss factor ($\tan \delta$) were recorded as functions of temperature. Samples of dimension 40 mm × 12 mm × 3 mm are used for the analysis.

Preparation of laminates

DABA: EPN: BMI blends with varying BMI concentrations were weighed in separate containers so as to have different BMI equivalent ratios 1 : 1 : B ($B = 0, 0.5, 1.0, 1.5, \text{ and } 2.0$). The mass of the glass fabric was calculated so as to give sufficient number of plies to give a reasonable thickness to the laminate (4–5 mm). A fixed mass of the matrix blend was taken so as to give the matrix to reinforcement volume ratio of 40 : 60. These mixtures were dissolved

in sufficient quantity of acetone (15 times the weight of resin blend). Glass fabric prepregs were prepared by dipping the fabric in solution and drying for 18 h at room temperature. These prepregs were cut into rectangular pieces of dimension 12 cm × 10 cm, stacked and molded in a hydraulic press between thick metallic plates to achieve desired thickness. The following cure schedule was adopted for the composite fabrication. The cure condition optimized for the matrix system was used for the composite and a pressure of 3.5 MPa was applied after the gelation of the resin at 150°C.

Temperature (°C)	100	150	200	250
Hold time (min)	60	30	60	300

Evaluation of adhesive properties

The high temperature performance of the EP and EPB matrix systems was evaluated by determining their adhesive properties at ambient and elevated temperatures (80, 100, and 120°C). The adhesive properties of the matrix system were evaluated by determining their lap shear strength as per ASTM D-1002. Chromic acid etched, B-51-SWP aluminum alloy strips of 25 mm × 150 mm were used as substrates. About 80% solution of the TPP catalyzed EPB blend was applied as a thin layer over the aluminum substrate. The solvent was allowed to evaporate by keeping the specimen in hot air oven at 75–80°C for 2 h. They were then allowed to cool to room temperature and assembled for curing at desired temperature in an air oven. The assembled specimens were subjected to a pressure of 0.5 MPa using a lever press assembly. The curing of the polymer blend was achieved by following the time–temperature cure schedule optimized for the EPB system. The bonded specimens were tested in an Universal Testing Machine-Instron-model 4202, at a crosshead speed of 10 mm/min. The adhesive properties were evaluated at higher temperatures by soaking the samples at the desired temperature in the Instron climatic chamber for 10 min prior to testing.

RESULTS AND DISCUSSION

Cure characterization of the ternary polymer blend

Differential scanning calorimetry

The reactive blend of DABA, EPN, and BMI underwent curing through reaction among the three components by a combination of phenol–epoxy and phenyl maleimide–allyl phenol reactions. The phenol–epoxy reaction shifted to a lower temperature regime on adding the catalyst (0.5%) TPP. This

reaction was investigated in detail separately and found that at 0.5% TPP level, the reaction becomes complete at 140°C.²¹ The reaction between allyl phenol and maleimide is well established through detailed spectral investigation on model compounds. The major reactions include an Ene reaction occurring at a temperature regime of 140–190°C. At higher temperatures and at higher proportions of phenyl maleimide, the Ene product undergoes Diels–Alder reaction with maleimide to generate crosslinked system. The maximum crosslinking occurs at an allyl phenol–phenyl maleimide molar ratio of 1 : 3.^{15,16} This cure chemistry has been substantiated in subsequent investigations involving various polymer systems bearing these functional groups.²² Hamerton extrapolated this cure chemistry to get allyl triazine–maleimide cocured matrix.¹⁷ It is generally accepted that the DSC exotherm initiated at around 140°C is due to the Ene reaction and that at 190°C is due to the Diels–Alder reaction. Extended Diels–Alder reaction occurs in some cases beyond 200°C.

In the present system, the DSC thermogram of the diallyl bisphenol A and epoxy manifested a single exotherm with T_{max} at 137°C attributed to the phenol–epoxy reaction.²³ The DSC of the ternary system of diallylbisphenol A-EPN and BMI manifested a thermogram whose profile matches with the reported cure sequences and temperature regions for phenyl allyl–bismaleimide system. The exception is the low temperature exotherm initiated at around 110°C. This is attributed to the phenol–epoxy reaction as evident from the DSC thermogram of DABA and EPN (Fig. 1). The cure reaction from 140 to 190°C is comprised mainly of the Ene reaction as reported previously.^{15,17} The one centered around 200°C can be

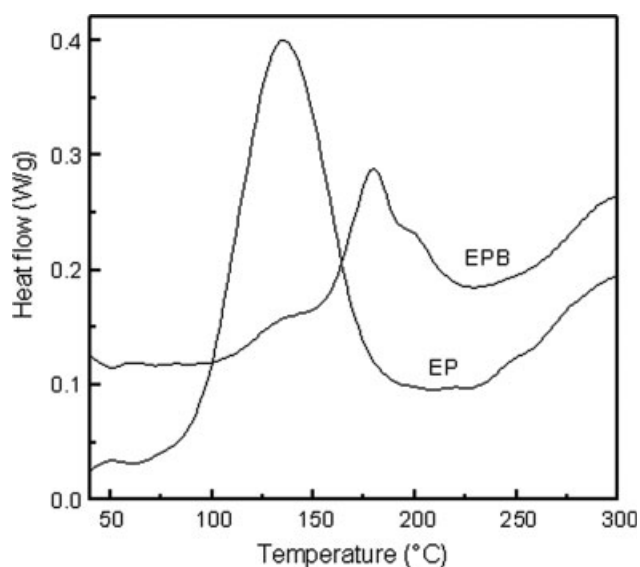


Figure 1 DSC plots of the EP and EPB systems (heating rate, 10°C/min).

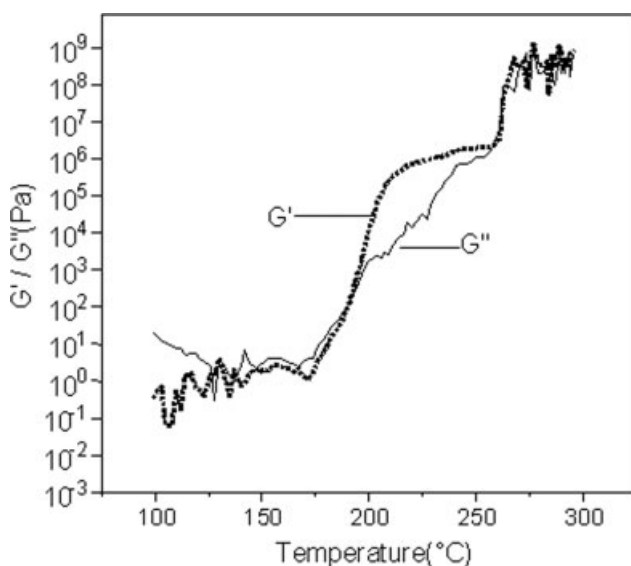


Figure 2 Temperature dependence of storage shear modulus (G') and loss shear modulus (G'') of EPB system (1 : 1 : 1). (heating rate, 5°C/min).

attributed to Diels–Alder reaction of the Ene adduct with BMI as reported in literature.^{15,18}

Rheological cure characterization of the blends

The rheological characterization of the resin blends gave an insight into the rate and extent of cure reaction with respect to temperature and time, which also enabled the optimization of processing window for composite fabrication.

The complex viscosity (η^*), storage shear modulus (G'), and loss shear modulus (G'') of the ternary blend were monitored as a function of temperature (T) using the rheometer. This enabled the determination of gel point, which is taken as the temperature corresponding to the crossover point of the G' and G'' curves.²⁴ The variation of G' and G'' with temperature for the EPB system is shown in Figure 2. Though the phenol-epoxy reaction sets in at $\sim 100^\circ\text{C}$, the resultant increase in shear modulus is negligible. The Ene-reaction, though initiated at $\sim 140^\circ\text{C}$, causes visible changes in modulus only in the temperature region 175–190°C. The Diel–Alder reaction at $\approx 200^\circ\text{C}$ causes further increase in modulus. Major cure reactions are completed by 200–210°C. The rheological analysis manifested a further crosslinking centered at 250°C. Earlier investigations have attributed it to the curing of the residual maleimide present in the system. Since the present resin blend contains less maleimide (ally phenol: maleimide ratio 1 : 1 instead of theoretically affordable 1 : 3), the possibility for residual maleimide is negligible. On the other hand, the polymer formed at 200°C contains unsaturated groups, which could undergo thermal polymerization at 250°C. In all probability, the curing at 250°C

can be attributed to this reaction. DSC data also showed a weak exotherm triggered at this temperature range. Thus, the rheological behavior conformed to the proposed reaction sequences. Hence, the isothermal rheological studies were carried out to optimize the cure time at 250°C.

The storage shear modulus of the EPB systems with different BMI concentrations under isothermal (250°C) condition is given in Figure 3. The G' curve showed a tendency to level off at about 300 min. The isothermal rheograms of the systems with varying BMI content revealed that the absolute modulus and its rates of build-up increases with the BMI content in the EPB system. The cure stagnation reaches at a lower time scale as the BMI concentration in the system is increased. The ultimate cure schedules were drawn based on these studies.

Characterization of the cured matrix system

IR spectroscopy

Spectroscopic studies using *N*-phenyl maleimide and 2-allylphenol as model for the chain extension and crosslinking reactions of thermal curing of BMI-DABA system have been reported.¹⁵ Also cure monitoring by IR of the BMI-Allyl phenol system has been done²⁵ by observing the changes in the peaks at 820, 915 and 1183 cm^{-1} assigned to maleimide C–H, allyl CH_2 , and ether C–O and hydroxyl (–OH) groups, respectively that are involved in the cure reaction. The IR spectra of the cured and uncured EPB matrix systems are shown in Figure 4.

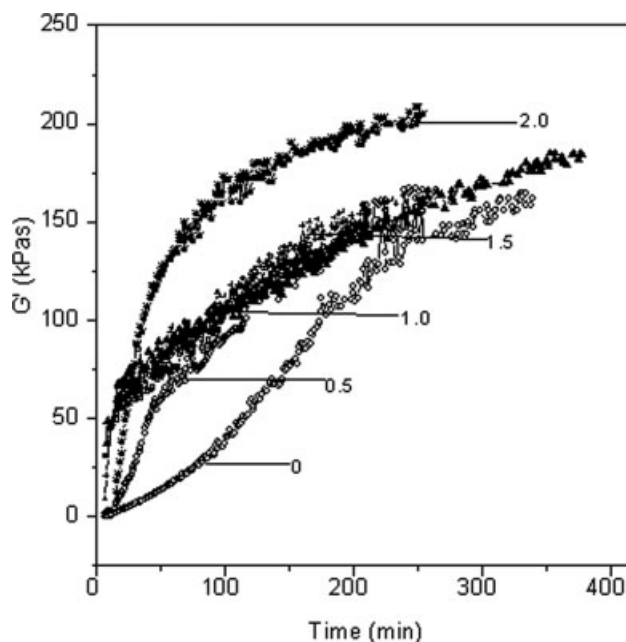


Figure 3 Isothermal (250°C) storage shear modulus (G') curves of EPB systems with varying BMI equivalent concentrations.

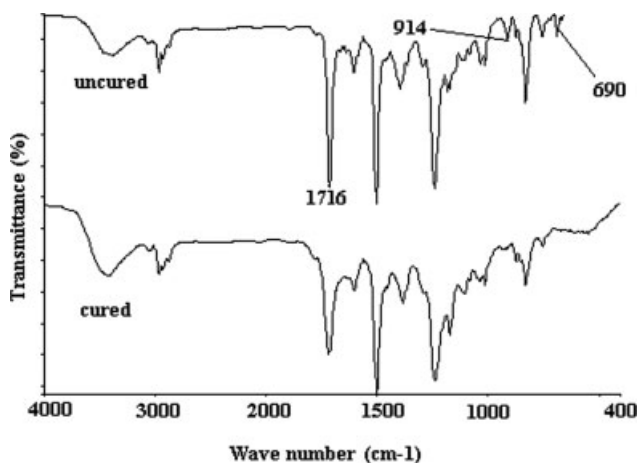
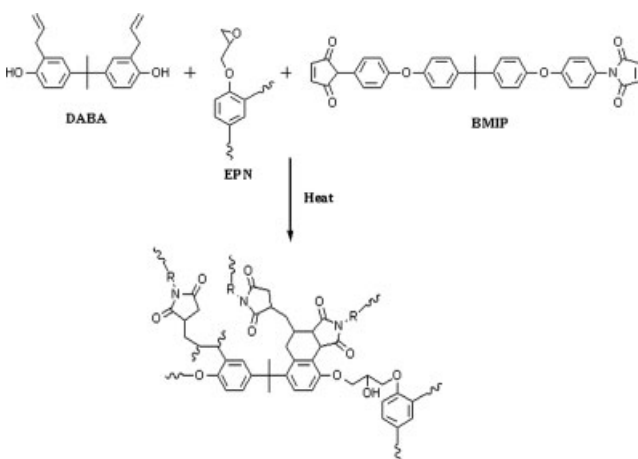


Figure 4 IR Spectrum of stoichiometric blend (1 : 1 : 1) of EPB system before and after curing.

The peaks at 690 cm^{-1} due to $=\text{C}-\text{H}$ bending of maleimide, that at 914 cm^{-1} due to both epoxy and allyl groups were found to disappear in the spectrum of the cured product confirming the curing. The peak at 1716 cm^{-1} due to $\text{C}=\text{O}$, decreased in intensity. This phenomena has been ascribed to the transformation of the α, β unsaturated $\text{C}=\text{O}$ groups in the monomer to the saturated one in the polymer.²⁶ Based on the evidence from the DSC, corroborated by rheology and further substantiated by IR analysis, it can be expected that the diallylbisphenol-DABA system cures by Alder-Ene reaction as has been established by previous studies. The presence of epoxy resin leads to an additional phenol-epoxy reaction occurring prior to or along with the Ene reaction. The phenol is transformed to a phenyl ether group. It has been reported that transformation of allyl phenol to allyl phenyl ether does not impede or alter the Alder-Ene reaction.^{17,18} Based on these evidences, the network structure of the EPB system cured at 250°C can be postulated as in Scheme 1 (for



Scheme 1 The reaction scheme of the EPB system.

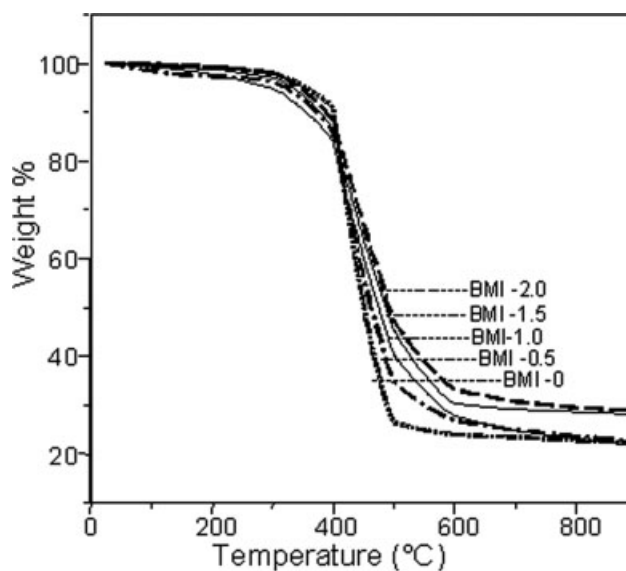


Figure 5 Thermograms of EPB systems with varying BMI concentrations in N_2 . Heating rate, $10^\circ\text{C}/\text{min}$.

a 1 : 1 : 1 matrix.). As the BMI concentration increases, more crosslinks will be generated through the Diels-Alder reaction.

Thermo gravimetric analysis

The thermograms of the cured EPB blends with varying BMI concentrations are shown in Figure 5. The dynamic mass-loss curves are seen to overlap at the peak decomposition temperature (TG_m), showing that the peak reaction temperatures are within a narrow range. The temperatures of initiation of reaction

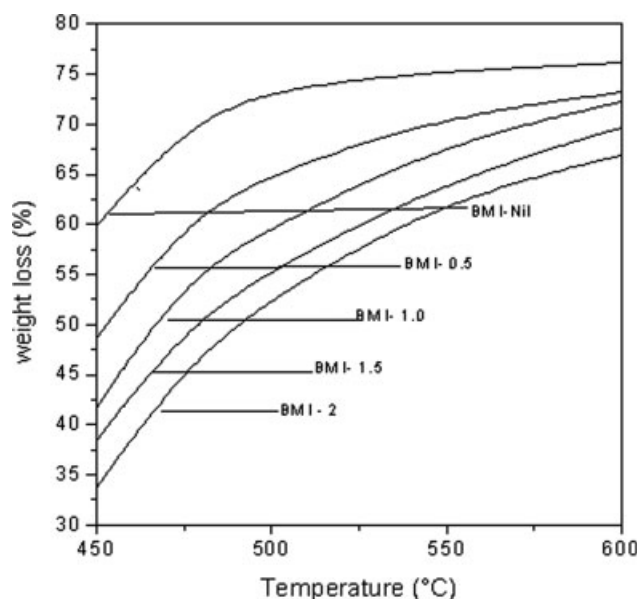


Figure 6 Effect of BMI concentration on the mass loss of EPB systems at different temperature.

TABLE III
Effect of BMI Concentration on the Decomposition Temperature of EPB Neat System

BMI equivalent ratio in EPB system	TG _i (°C)	TG _m (°C)	TG _c (°C)	Residue at 600°C (%)
0	230	430	605	24
0.5	233	430	620	27
1.0	229	430	637	28
1.5	230	428	658	30
2.0	234	421	679	33

Heating rate: 10°C/min in N₂.

(TG_i) are not altered much by the increase in BMI concentration in the blend. However, at temperatures above TG_m, the concentration of BMI in the blend was found to influence the mass-loss rate. The temperature of completion of decomposition reaction (TG_c) showed a systematic increase with increase in BMI concentration. The residual mass was found to be more for the system with high BMI content. This trend is clearly shown in Figure 6, which indicates that the mass-loss at temperatures above TG_m is more pronounced for BMI-starved matrices. Similar observations were made earlier for the kinetic studies carried out on the amine cured epoxy-bismaleimide blend.¹⁰ The peak reaction temperature indicated a marginal lowering tendency at high BMI concentration in the blend. This is a result of the increased concentration of aliphatic groups originated from the Alder–Ene reaction (Table III).

Dynamic mechanical thermal properties

The dynamic mechanical thermal analysis (DMTA) was performed on the glass laminates of the EPB matrix system of varying BMI concentrations. The

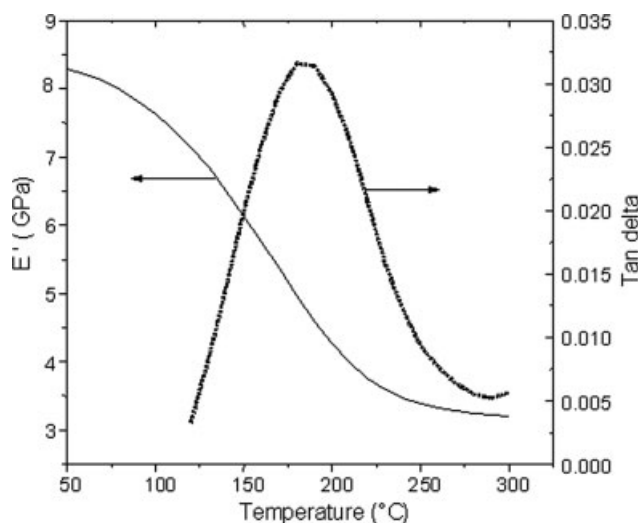


Figure 7 Typical DMTA thermogram of 1 : 1 : 1 EPB composite. Heating rate, 10°C/min.

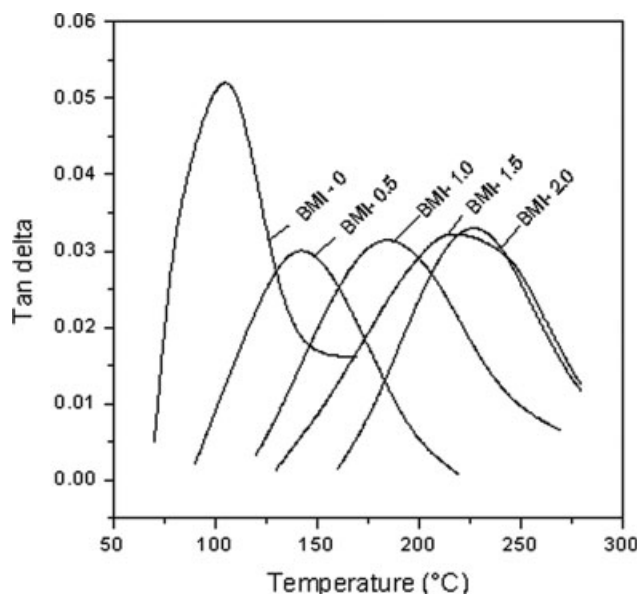


Figure 8 Effect of BMI concentration on the tan δ of EPB composite.

modulus values obtained from dynamic mechanical analysis is of obvious importance for the use of polymers for structural applications. Of great importance is the information provided by damping since the end use properties—vibration dissipation, impact resistance, and noise abatement—are all related to mechanical damping.

The DMTA analysis was carried out in flexure mode and the storage modulus (E'), loss modulus (E''), and tan δ of the samples were recorded as a function of temperature. The typical DMA curves of the EPB (1 : 1 : 1) composite are shown in Figure 7. The tan δ peaks of the EPB composites with varying BMI concentrations obtained from the DMA thermograms are shown in Figure 8. The dynamic mechanical thermograms indicated a shifting of the tan δ peaks to higher temperature, indicating a systematic increase in T_g of the system with BMI concentration in the ternary blend. The T_g values are included in Table IV. Figure 9 gives the effect of temperature on the storage modulus of the EPB composites with different BMI concentrations. The modification of EP system using BMI was found to enhance its storage modulus. The mechanical properties of the composites of this matrix system will be detailed in an ensuing publication.

TABLE IV
Effect of BMIP concentration in the EPB system on its glass transition temperature

BMI equivalent ratio in EPB system →	0	0.5	1.0	1.5	2.0
T _g (°C)	106	143	184	215	225

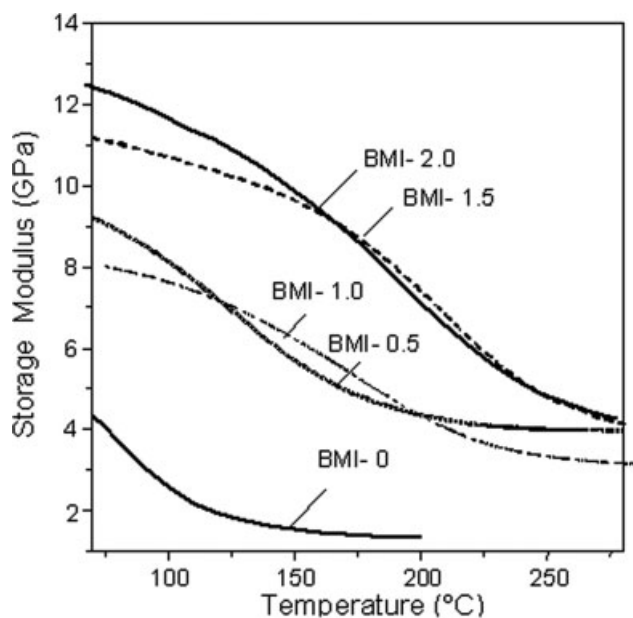


Figure 9 Effect of BMI concentration on the storage modulus the EPB composite.

Cole-cole plots

The storage modulus was plotted against $\tan \delta$ obtained for the 1 : 1 : 1 stoichiometric blend of the EPB composite system to get the Cole-Cole plot. For perfectly elastic system, the plot is supposed to be an inverted semi circle. The plot obtained for the EPB system (Fig. 10) showed that the system behavior is close to that of elastic material.

Lap shear strength evaluation

The high temperature performance of the EPB system was evaluated typically from the high tempera-

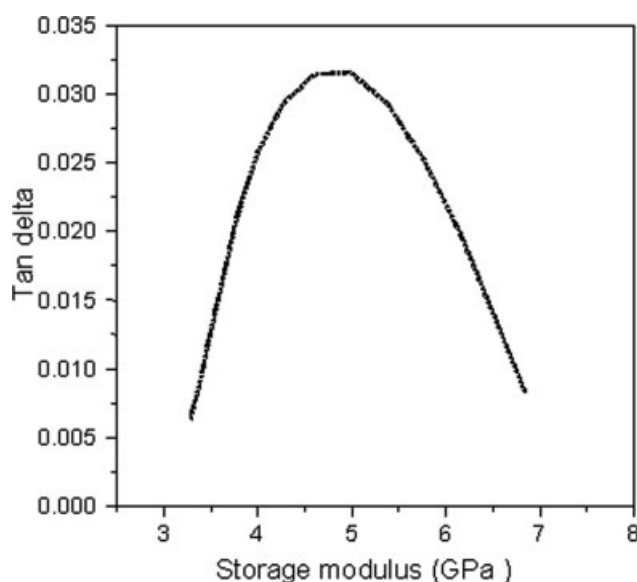


Figure 10 Cole-Cole plot of the 1 : 1 : 1 EPB composite.

TABLE V
Adhesive Strength Properties of EP and EPB Systems at Different Temperatures

	EP system (1 : 1)			EPB system (1 : 1 : 1)			
Test temperature (°C) →	RT	80	100	RT	80	100	120
LSS (kg/cm ²)	210	150	30	190	180	185	150

ture lap shear strength (LSS) of the matrix. The LSS of the EP(1 : 1) and EPB (1 : 1 : 1) systems were determined at ambient conditions and at elevated temperatures (80, 100, and 120°C) and the values are reported in Table V. The results indicated comparable strength properties for EP and EPB systems at ambient conditions. At higher temperatures, performance of the EPB system showed drastic improvement. The considerable increase in glass transition temperature observed for the EPB system was reflected in its remarkable strength retention at high temperatures.

CONCLUSIONS

The reactive blending of bismaleimide to an epoxy-allylphenol system provided a cocured matrix system with improved high temperature resistance in comparison with the epoxy-phenol system. The system cured through a multitude of reactions characteristic of epoxy-phenol and allyl phenol-BMI as evidenced from the DSC, FTIR, and rheological analyses. The presence of bismaleimide in the blend led to an increase in glass transition temperature and stiffness of the EPB-glass composite. Though the initial decomposition temperature was practically unaffected by BMI, it was conducive to reducing the rate of thermal erosion at higher temperatures. The improved high temperature performance of the EPB matrix system was indirectly concluded from the retention of LSS of the system at high temperatures.

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