

Blends of Bisphenol A-Based Cyanate Ester and Bismaleimide: Cure and Thermal Characteristics

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ABSTRACT: A dicyanate ester, namely, 2,2-bis-(4-cyanatophenyl)propane, and a bismaleimide, namely, 2,2-bis[4-(4-maleimido phenoxy)phenyl]propane, possessing closely resembling backbone structures, were cured together to derive bismaleimide–triazine network polymers of varying compositions. The blend manifested a eutectic melting behavior at a 1 : 1 composition with a eutectic melting point of 15°C. The cure characterization of the blends was done by DSC and dynamic mechanical analyses (DMA). The near simultaneous cure of the blend could be transformed to a clear sequential one by catalyzing the dicyanate cure to lower temperature using dibutyl tin dilaurate. The two-stage, independent cure of the components of the blend evidenced in DSC was confirmed by DMA. The cure profile of the bismaleimide component predicted from the kinetic data derived from nonisothermal DSC was found to be in league with the isothermal DMA behavior. Both techniques led to optimization of the cure schedule of the blends. The cured polymers were characterized by FTIR and TGA. The cured blends underwent decomposition in two stages, each corresponding to the polycyanurate and polybismaleimide. Enhancing the bismaleimide component did not alter the initial decomposition temperature, but led to reduced rate of thermal degradation at higher temperature. Interlinking of the two networks and enhancing crosslink density through coreaction of the blend with 4-cyanatophenylmaleimide unaffected the initial decomposition properties but was conducive for increasing the char residue significantly. Computation of activation parameters for the thermal decomposition of the polymers confirmed that the first step in the degradation of the blends is caused by the polycyanurate component. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3365–3375, 1999

Key words: bisphenol A dicyanate; bisphenol A bismaleimide; B-T resins; sequential IPN; thermal cure; cure kinetics; network interlinking; cyanatophenylmaleimide; thermal decomposition kinetics

INTRODUCTION

Polycyanurates derived from the thermal cure of dicyanate esters possess several edges over the state-of-the-art polymer matrices such as epoxies

and bismaleimides.^{1,2} They possess the good physical, dielectric, and mechanical properties required of an ideal matrix resin in structural composites for aerospace applications. However, the thermal characteristics are inferior to those of bismaleimide resins. The latter system dominates over the epoxy-based structural polymer matrix composites, owing primarily to their high performance-to-cost ratio and relatively high tempera-

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ture resistance.³ However, their processability is difficult and their fracture toughness is not good. Cyanate esters, on the other hand, have epoxylike processability and excellent toughness. However, their thermal stability is marginally inferior to that of bismaleimides.

One apparent method to derive both thermal stability and processability is to realize a blend of the two resins. Such blends could also possibly benefit from the good physicochemical attributes of the two systems. Blends of BMI and cyanate esters (CE) have already been reported. Commercial blend formulations of bismaleimide–cyanate, known as B–T resins such as Skyflex® of Mitsubishi Gas Chemical Co., are available.^{4,5} Several patented B–T resin formulations are claimed which find applications as engineering materials in aircraft, reinforced plastics, and injection-molding powders and as materials in high-speed circuits, in electric motor coil windings, etc.^{6,7} With attractive properties such as reduced moisture absorption, chemical resistance, dimensional stability, insulation, and low dielectric constant, they are preferred in circuit boards and semiconductor encapsulants.

It was postulated that in such blends the two resins coreact during curing but without much proof for the resulting pyrimidine structure. Lack of support for the coreaction has now led to the conclusion that the two systems form an interpenetrating polymer network (IPN)⁸ and not a co-cured matrix.⁹ Allyl functional cyanate esters are added to promote the coreaction and thereby to facilitate partial homogenization of the linked B–T IPN matrix with concomitant improvement in the T_g .¹⁰ A related patent application describes the synthesis of molecules with both cyanate and maleimide functions and their effect on the mechanical properties of a few molding compositions containing BACY or its blend with styrene or ethyl hexyl acrylate, etc.¹¹ In the very little published literature on B–T resins, there has been practically no study on the detailed mechanical characteristics of such blends.

The objective of the present work was to examine the blend or possibly the IPN of a commercial dicyanate ester and a relatively tougher bismaleimide, both possessing a closely resembling backbone structure based on bisphenol A. The components of the blends are 2,2-bis-(4-cyanatophenyl)propane, known also as bisphenol A dicyanate (BACY), and 2,2-bis [4-(4-maleimido phenoxy)phenyl]propane (BMP), known also as bisphenol A bismaleimide (structures in Scheme 1). The

former is a versatile commercial cyanate ester monomer. The bismaleimide has been relatively less studied. It is a low melting solid and affords a network with reduced brittleness thanks to the phenyl ether spacing between the two maleimide groups. The structural similarity is expected to facilitate good miscibilization and, thereby, to reduce the probability of phase separation in the cured IPN network. This article describes the cure characterization of the blend for optimizing the cure conditions. The cure kinetics of the bismaleimide component were analyzed. The thermal characteristics of the blend and the effect of a network linking agent on it was examined.

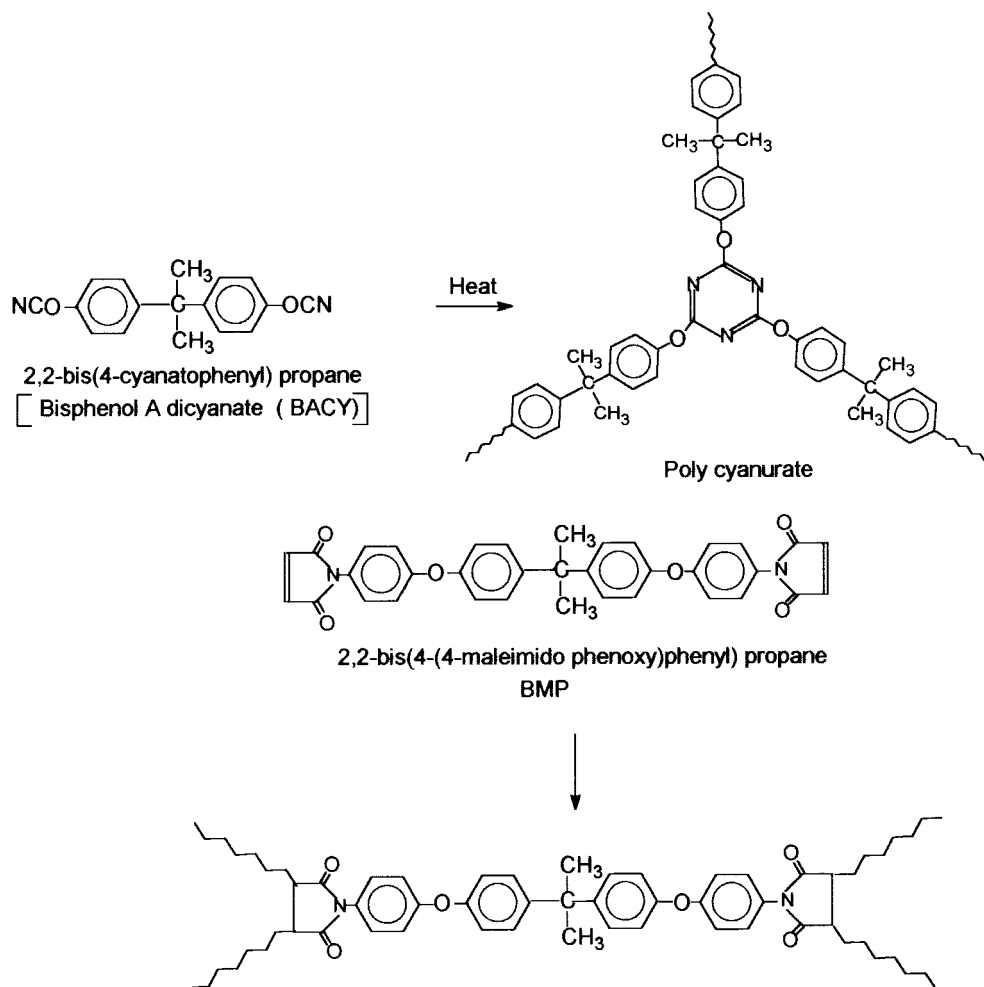
EXPERIMENTAL

Materials

BACY was synthesized from bisphenol-A by reaction with cyanogen bromide in CCl_4 in the presence of triethylamine at -30°C .¹² The product was recrystallized from cyclohexane. Yield = 80%, mp = 79°C . BMP was a gift sample received from Mr. T. M. Vijayan (VSSC) who synthesized it by modification of a reported procedure.¹³ *p*-Cyanatophenylmaleimide (*p*-CPM) was prepared from *p*-maleimidophenol and cyanogen bromide by a method described by Mathew.¹⁴ The *p*-maleimidophenol required for the synthesis of *p*-CPM was, in turn, prepared from *p*-aminophenol (E-Merck, Germany) and maleic anhydride (CDH, Agra, India) by a reported procedure.¹⁵ All solvents used were of reagent grade. Silane-treated, plain-weave E-glass of 7 mil thickness (Unnathi Corp., India) was used for resin impregnation for DMA studies. Dibutyl tin dilaurate (DBTDL, E-Merck, Germany) was used as received.

Instruments

Dynamic DSC was performed at $10^\circ\text{C}/\text{min}$ in static air using a Mettler TA 3000 thermal analyzer system in conjunction with a TC-10ATA processor and a standard DSC-20 apparatus. The temperature and heat-flow calibrations were done by the recommended procedure using pure indium metal with a melting point 156.4°C and a heat of fusion, ΔH_f , of 6.80 cal/g. The enthalpy of curing, ΔH , was determined from the area under the exothermic peak and the sample mass. The peak area integration and subsequent fractional conversion (α)–temperature calculations were



Scheme 1 Structure of components of blend and mechanism of polymerization.

done by a Mettler graphware TA 72 AT.2 software. Conversion at any temperature, α_T , was found from the relation $\alpha_T = \Delta H_f / \Delta H_T$, where ΔH_f is the fractional enthalpy at that temperature, and ΔH_T , the total heat of the reaction. Indirectly, these are obtained by the fractional and total areas, respectively, under the exothermic curve.

FTIR spectra were recorded with a Nicolet 510 P instrument. Thermogravimetric analysis was performed on a DuPont 2000 thermal analyzer in conjunction with a 951 thermogravimetric analyzer in an argon atmosphere at a heating rate of 10°C/min over the temperature range from 30–700°C. Dynamic mechanical analysis (DMA) was performed using a DuPont DMA-983 in a nitrogen atmosphere at a frequency of 1 Hz. Single-ply prepreg was used for cure characterization by DMA analysis.

Melting Point

The melting points were determined by the capillary method and are uncorrected. The monomer mixture was homogenized by melting them together, mixing, and then cooling.

Prepolymerization Studies

The blends of BACY and BMP in different proportions (along with *p*-CPM in relevant cases) were melted separately and thoroughly mixed at 120°C. The liquid mixture was deaerated under a vacuum at this temperature for 45 min. The temperature was lowered to 100°C and DBTDL (0.1% by weight of BACY) was added to the mixture and mixed well. Samples for IR analysis (neat) were withdrawn at different time intervals and the resin consistency was noted visually.

Polymerization

The prepolymerized blends were poured into an aluminum mold and cured by stagewise heating in an air oven. The polymerization was done at 150°C for 90 min and at 220°C for 1 h. The formed slab was taken out and further cured at 250°C for 3 h in a free-standing mode. BACY was polymerized the same way. BMP was polymerized under the same cure schedule, but without any catalyst.

RESULTS AND DISCUSSION

Although polycyanurates derived by the thermal cure of cyanate esters have many attractive physical, electrical, and mechanical properties, their thermal stability and thermomechanical profile are inferior to those of conventional bismaleimide systems. Blends of the two have been realized to derive systems possessing the thermal characteristics of BMI and the toughness of polycyanurates. The IPN formed in these cases have been found to exhibit two T_g 's and the use temperature of the blend is limited by the low T_g system.^{10,16,17} The two T_g 's result due to microphase separation caused by the two incompatible polymers. One way to obviate this is to derive a B-T blend from components having close solubility parameters. Thus, in this study, a B-T system comprising polycyanurate derived from BACY and polybismaleimide formed from BMP was attempted. The solubility parameter (δ) calculated for the former polymer is $22.0 \text{ J}^{1/2} \text{ cm}^{-3/2}$ and that for the latter polymer is $22.4 \text{ J}^{1/2} \text{ cm}^{-3/2}$. The closely matching δ values ensures, *a priori*, a compatible blend. The reported B-T systems contains bismaleimide with a very high crosslink density such as bis(4-maleimidophenyl)methane or naphthalene-based bismaleimides with inherent rigidity.¹⁸ The present study used BMP as a bismaleimide component whose structural feature provides relatively lower crosslink density (than the previously used BMI components) in the network to be formed. Considering the idealized structures for the infinitely crosslinked BMP and BACY, the theoretical crosslink density (in terms of number of crosslinks per unit volume) is $2.2 \times 10^{-3}/\text{cc}$ for the former and $1.5 \times 10^{-3}/\text{cc}$ for the latter. The calculation shows that cyanate ester has comparatively less crosslink density.

Prior to molding the blends of varying compositions and examination of their mechanical and physical properties, it was imperative to study

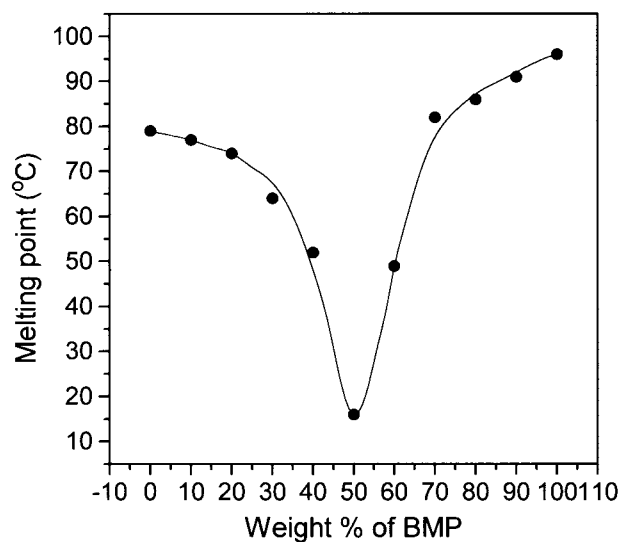


Figure 1 Variation of melting point with blend composition.

their cure characteristics in order also to ascertain the nature of the possible network formed and to optimize the conditions for deriving them. The cure characterization of the blend was investigated by a combination of DSC, DMA, and FTIR. The variation in melting point of the monomer mixture with composition is shown in Figure 1. The eutectic melting point of 15°C results for the 50/50 mixture (weight percent). The low melting points of the mixtures ensures easy resinification, impregnation of reinforcement, and molding of the blends.

Cure Characterization

Figure 2 shows the DSC thermograms of the two monomers and their mixtures. BACY starts curing at 225°C with a maximum at 275°C, the cure ending at 320°C. The corresponding temperatures for BMP are 260, 300, and 340°C. On blending the two, the cure spreads over a wider temperature range [Fig. 2(C)]. Minor curing starts at 170°C with the peak at 270°C and the cure ends at 320°C. The low-temperature cure is contributed by the cyanate ester catalyzed by impurities (traces of amic acid, etc.) present in BMP. When molding of the blend was attempted by thermal curing at 250°C, the system required several hours for consolidation and the "cured" sheets were not perfect and, at times, were soft, indicating incomplete cure. Hence, the dicyanate cure was advanced by addition of DBTDL, a known

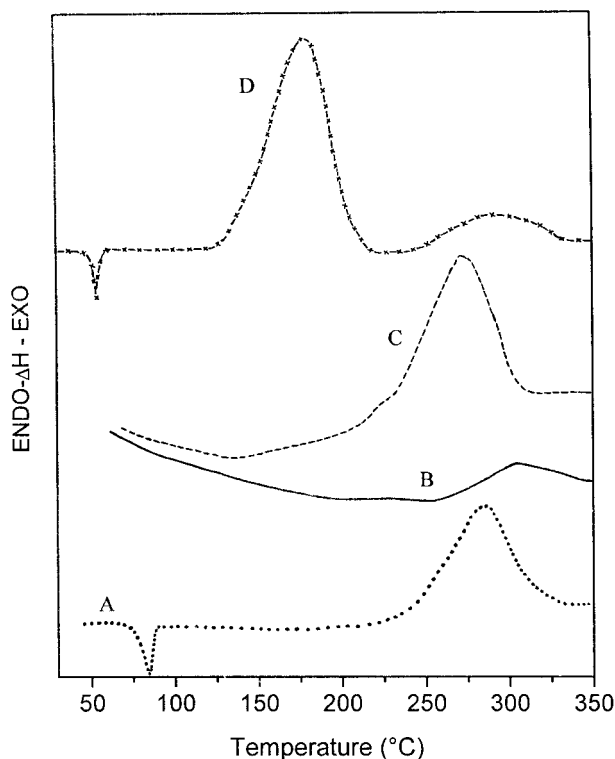


Figure 2 DSC thermograms of (A) BACY, (B) BMP, (C) BACY/BMP-60/40, and (D) BACY/BMP-60/40 with DBTDL.

catalyst for its cure.¹³ Although systems such as cobalt naphthanate, zinc octoate, etc., in combination with nonylphenol are the commercially used catalysts, we found that DBTDL is an equally good catalyst for cyanate curing, leading to polycyanurates with the same characteristics as those obtained using the other catalysts.^{13,14} It has the added advantage of easy dispersion in the BACY matrix, unlike the other catalysts which require a cocatalyst like nonylphenol for facilitating the dispersion of the catalyst.

The DSC thermogram given in this case in Figure 2(D) shows a clean shift of the BACY cure to lower temperature. The BACY cure is initiated at 120°C and ends at 215°C with a peak maximum at 198°C, while the cure profile of BMP remains practically unaltered. The two-stage curing of the blend shows that the dicyanate and bismaleimide polymerizes independently and, consequently, the resultant system has to be an IPN (if not phase-separated) and not a cocured system, in line with the observation of Gaku⁹ and Barton et al.¹⁶ The independent curing was also evidenced from the measurement of the heat of polymerization of the bismaleimide as estimated

from the DSC analysis of the mixture and that of the pure bismaleimide (i.e., BMP). The ΔH of BMP was estimated as 129.4 J/g. The ΔH value for cure of BMP in its 40% mixture (by weight) was estimated as 48 J/g as against the theoretical value of 51.6 J/g, which are a close match. The possibility for error in the estimation of the low ΔH value was associated with the bismaleimide cure. The DSC shows that the cure of dicyanate is completed at around 210°C before the maleimide starts polymerizing. Thus, the sequential polymerization of the components implies that the polymer derived under this cure condition is most likely to be a sequential IPN of polycyanurate and polybismaleimide. The catalyst is active only with respect to the cyanate ester whose polymerization is practically completed at lower temperature in comparison to that of the bismaleimide component.

The catalyzed cure of the BACY component helps gelation and consolidation of the blend system at lower temperature and facilitates its molding. In the absence of added catalysts, the blend was found not to consolidate perfectly even after curing for hours at higher temperature. The early gelation of the cyanate ester component is particularly helpful in preventing the resin bleeding at higher temperature during fabrication of composites of the blend. For further polymerization studies, DBTDL was employed as a catalyst at a concentration level of 0.1% by weight of the dicyanate ester.

Prepolymerization of Cyanate Ester

It was found that good, homogeneous, molded plaques can be obtained if the polymerization of the mixture is carried out in steps of increasing temperature. This provides good control over the system and helps avoid the otherwise violent polymerization of the cyanate component. Best results were obtained when the monomer mixture was partially polymerized prior to pouring into the mold. The system was, hence, partially, polymerized at 100°C. Only the cyanate component is expected to polymerize at this temperature in the presence of the catalyst. The extent of cyanate conversion was estimated by an FTIR technique by monitoring decrease in the intensity of the absorption at 2237 cm^{-1} due to the OCN groups vis-à-vis the absorption at 2970 cm^{-1} due to the CH_3 group considered as an internal standard. The time-conversion plot in this case is shown in Figure 3. The prepolymerization was continued

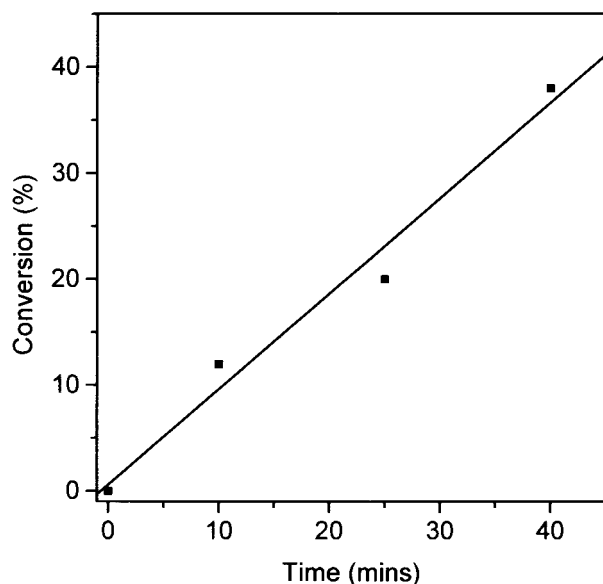


Figure 3 Time-conversion plot for prepolymerization of BACY in the blend at 100°C.

for 40 min, during which 38% of the cyanate function polymerized. The blend at this stage possessed a good resinous consistency and pourability at 100°C. The system contains oligomerized BACY with BMP monomer dissolved in it.

Kinetics of Polymerization of BMP Component

The DSC analysis shows that, under the dynamic conditions employed, the bismaleimide polymerization is complete at 340°C. This, *a priori*, warrants a higher cure temperature for the BMP component in order to realize a fully cured network. However, previous studies on other thermosetting resins have shown that the system can be fully cured at a relatively lower temperature than indicated by DSC.^{19,20} A first approximation of the isothermal cure profile can be obtained by estimation of the kinetic parameters from the dynamic cure.²⁰ Under non-isothermal conditions, the rate expression for polymerization is given as

$$d\alpha/dT = (A/\phi)e^{-E/RT} (1 - \alpha)^n \quad (1)$$

where α is the fractional conversion at temperature T , following a heating rate ϕ . E is the activation energy, and A , the Arrhenius frequency factor. The order of reaction is n .

Several integrated forms of the above equation have been used for evaluation of the kinetic pa-

rameters. The most versatile one is the Coats-Redfern equation²¹ (C-R) given as

$$\ln\{g(\alpha)/T^2\} = \ln\{(AR/\phi E)(1 - 2RT/E)\} - E/RT \quad (2)$$

where $g(\alpha) = \{1 - (1 - \alpha)^{1-n}\}/(1 - n)$; for $n = 1$, $g(\alpha) = -\ln(1 - \alpha)$; and R is the gas constant. The fractional conversion α is found from the DSC curve from the fractional and total enthalpy of cure, both obtained by dedicated software as explained in the Experimental section. Data were taken from the DSC curve shown in Figure 2(D).

The above equation was applied to derive the kinetic parameters for the cure of the BMP component in the blend. The order of the reaction was found from the best-fit linear plots of $\ln\{g(\alpha)/T^2\}$ against $1/T$ for different values of n as per eq. (2). A typical kinetic plot for the determination of n is given in Figure 4. The value of n was obtained as 2. The other kinetic constants (E and A) were determined from the linear plot using eq. (2) for $n = 2$.

E was calculated as 171.5 kJ/mol, corresponding to $A = 8.22 \times 10^{13} \text{ S}^{-1}$. The E value is higher than that estimated for the thermal polymerization of other bismaleimides by the dynamic DSC method as reported by Hong et al.²² However, the higher activation energy in the present case is kinetically compensated by a higher frequency factor. The value reported by Hong et al. corresponds to the overall kinetics of the simultaneous

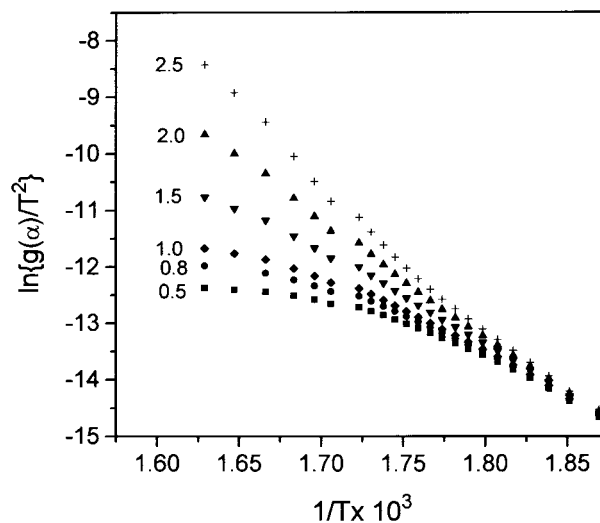


Figure 4 Determination of reaction order and activation parameters for the thermal cure of BMP from DSC.

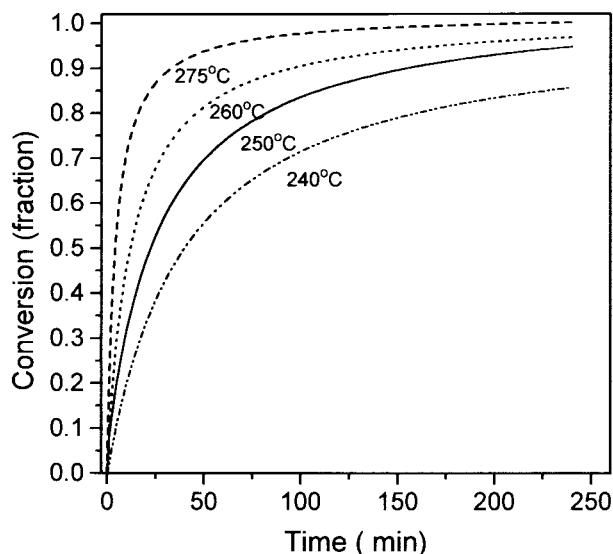


Figure 5 Predicted time-conversion profile for the thermal cure of BMP at different temperatures.

cure of BMI and BACY assuming coreaction between the two. From the kinetic constants obtained from the dynamic DSC, it was possible to predict the isothermal cure of the bismaleimide at different temperatures using the relationship

$$\alpha = 1/\{(1 - \alpha) (1 - n)te^{-E/RT}\}^{1/1-n} \quad (3)$$

The time-conversion profile predicted using the above equation for four different temperatures is given in Figure 5. The prediction reveals that a considerable extent of cure takes place in about 100 min at 250°C and that the cure attains near completion in about 3 h at this temperature.

Cure Characterization by DMA Analysis

DSC cannot be fully relied upon for following thermal polymerizations, particularly when such reactions are accompanied by only minor enthalpy changes as in the case of bismaleimides. In that case, it can be supplemented by DMA analysis. Since the uncured resins could not be served as specimens for DMA, they were indirectly evaluated using their glass fabric prepregs. The cure data derived from this can also be served for optimization of the cure during fabrication of their composites. The dynamic DMA of a 60 : 40 (BACY : BMP) mixture is shown in Figure 6, which confirms the two-stage curing detected in DSC. The first stage, corresponding to cure of BACY, sets off at 150°C and is nearly complete at 220°C. As the

glass transition of the cured cyanate ester starts manifesting (by a diminution in E'), the BMP starts curing at 250°C (E' increases) and its cure is completed at 325°C when the storage modulus stagnates. To minimize the possibility for thermal degradation of the polycyanurate during high-temperature cure of the BMP component, the final cure temperature of the blend was selected as 250°C. In another DMA analysis, the prepreg was heated under dynamic conditions until 250°C and then its isothermal curing at this temperature was monitored. The DMA shown in Figure 7 shows that E' stagnates in about 3 h on isothermal heating at 250°C, indicating completion of the cure during this interval. This suggested a cure time of a minimum of 3 h at 250°C for the blends, which was adopted for the final cure of all the blends. The DMA observation is quite in league with the kinetic prediction from DSC done above. It may be noted that the BMP cure is evidenced more in DMA than in DSC. The former technique detects even a minor cure at the end of the reaction, since it is associated with a significant change in the modulus and which is not sensed in DSC as the associated enthalpy change is negligible.

The two-stage curing, vaguely detected in DSC and clearly manifested in DMA, rules out the possibility for coreaction between the two systems. It may be remarked that this observation substantiates the earlier conclusions that the BMI-cyanate blend cures independently.^{9,16} Since the curing takes place independently and in sequence, the system may be classified as a sequential IPN in the absence of phase separation (to be proven in an ensuing publication). The cure mechanism and the possible network structure are shown in Scheme 1. The dicyanate polymerizes to

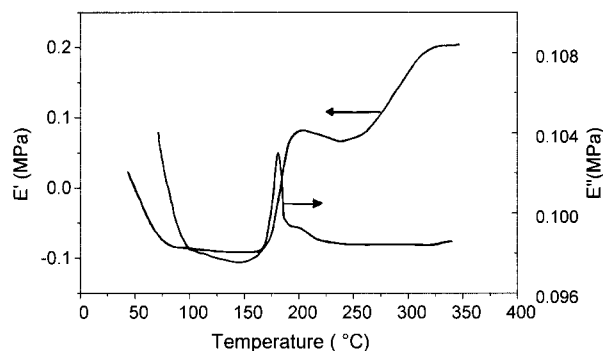


Figure 6 Cure characterization by nonisothermal DMA for the BACY/BMP 60/40 blend at 1 Hz. Heating rate: 2°C/min, in N_2 .

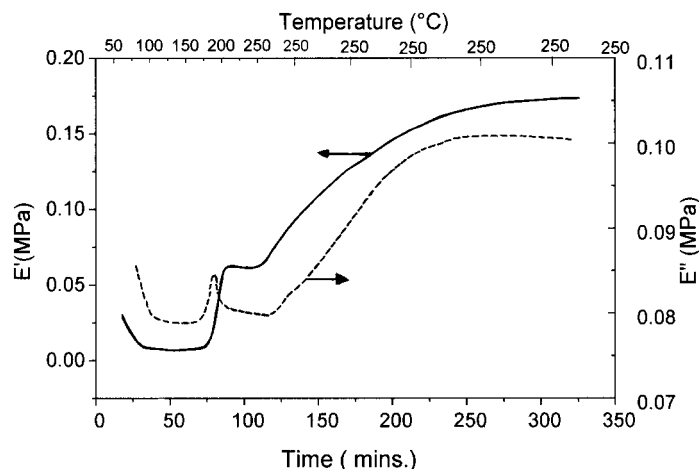


Figure 7 Cure characterization by isothermal DMA (at 250°C) for BACY/BMP 60/40, at 1 Hz. Heating rate: 2°C/min, in N₂.

the polycyanurate and BMP to the polybismaleimide independently.

Characterization of the Cured Blends

FTIR Analysis

The prepolymerized blends were cured by step-wise heating to 250°C and then postcuring at this temperature for 3 h. The completion of the cure of the blend was evidenced also in the FTIR spectra of the cured product. The spectrum of the uncured monomer mixture (given in Fig. 8) showed typical doublet absorption due to the OCN group at 2276 and 2235 cm⁻¹ which disappeared in the cured product to give rise to the triazine with its characteristic absorptions at 1370 and 1505 cm⁻¹. The characteristic absorptions due to the =C—H bending vibrations of maleimide which appeared at 690 cm⁻¹ in the monomer blend disappeared in the cured product, confirming the complete cure of the maleimide groups. The other notable changes are decrease in the intensity of the imide carbonyl absorption at 1730 cm⁻¹ (relative to other absorptions) on transforming maleimide to succinimide in the polymer. The peak at 827 cm⁻¹ attributable to the out-of-plane bending of the =CH group of the maleimide moiety showed a decrease in intensity on polymerization. This peak did not disappear completely in the spectra of the cured polymer because of concomitant absorption due to the out-of-plane bending vibration of other C—H groups (aromatic) at the same frequency.

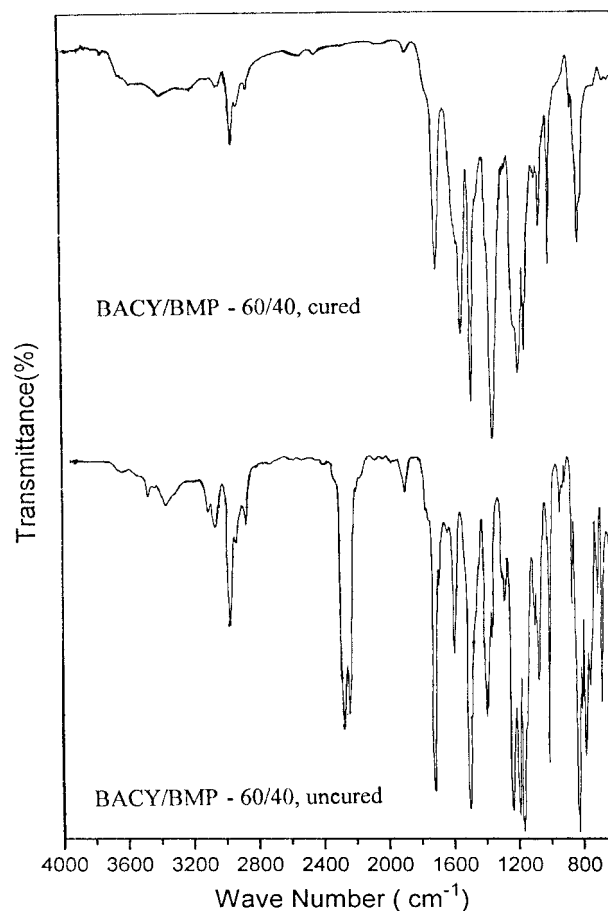


Figure 8 FTIR spectra of monomer mixture (smearred on NaCl) and cured polymer (KBr pellet) for the BACY/BMP 60/40 blend.

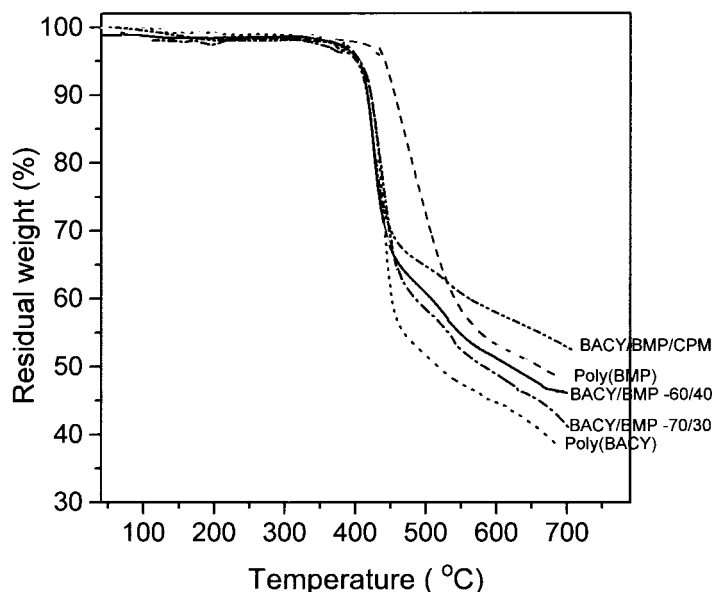


Figure 9 TGA thermograms of the homopolymers and cured blends in argon. Heating rate: 10°C/min.

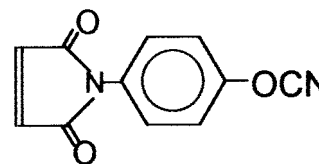
These changes are noticeable in the FTIR spectra of the monomer blend and that of the cured resin given in Figure 8. Minor absorptions were located in the region 3300–3600 cm^{-1} of both the cured and uncured monomer mixtures. It is partly contributed to by the minor amount of amic acid impurity (uncyclized compound) present in the bismaleimide and partly by the moisture incorporated while handling the samples. These impurities may be reacting with cyanate ester groups, leading to formation of some carbamate and imino groups which account for the slightly enhanced absorptions at this region in the cured product. However, their concentration is negligible to cause any significant change in the properties of the cured polymer.

Thermogravimetric Analysis

The thermograms of pure polyBMP, polyBACY, and typical blends are shown in Figure 9. The polybismaleimide clearly showed its superior thermal stability over the polycyanurate with a margin of about 30°C in the initial decomposition temperature (T_i). The char residue at 700°C was also higher for the former by about 10%. The blends showed two-stage decomposition. Their decomposition was initiated at the same temperature as for the pure polycyanurate. This was followed by the decomposition of the bismaleimide component, showing that the two components of

the blend decomposed almost independent of each other. Naturally, the mass loss in the first stage corresponding to the polycyanurate decreased and the anaerobic char residue increased on enhancing the maleimide content in the blend. In one case, *p*-CPM, possessing both cyanate and maleimide groups (see Scheme 2), was added at a concentration of 20 phr to the BACY/BMP 70/30 (BACY/BMP/CPM in Table I) blend with a view to interlink the two networks, since it is capable of reacting with both the components.

An earlier study reported the use of bisallyl dicyanate as a network linker on a polycyanurate–polybismaleimide IPN and was found to enhance the T_g while retaining the fracture characteristics, particularly in unidirectional composites.¹⁰ A patent application described the superior thermal characteristics of a polymer of *m*-cyanatophenylmaleimide over poly(BACY).¹¹ Cocuring of 4-[1-(*p*-maleimidophenyl)-1-methylethyl]phenylcyanate (possessing both cyanate and maleimide groups) with BACY resulted in marginal



Scheme 2 Structure of *p*-CPM.

Table I Thermal Decomposition Characteristics of the Homopolymers and Blends

Polymer System	T_i (°C)	Tlend (°C)	Residue at Tlend (%)	Residue at 700°C (%)	Kinetic Parameters ^a		
					Mass-loss range (%)	E (kJ/mol)	A^a (S ⁻¹)
Poly(BMP)	430	570	56.2	48	97–88, step I 88–61, step II	209 ± 2 89.4 ± 2	1.5 × 10 ⁹ 1.9 × 10 ¹¹
BACY/BMP 60/40	400	460	65	46	93–83	230 ± 2	2.6 × 10 ¹¹
BACY/BMP 70/30	402	473	61	42	93–82	248 ± 4	1.3 × 10 ¹³
BACY/BMP 80/20	400	455	63	41	93–84	240 ± 3	1.5 × 10 ¹²
Poly(BACY)	404	458	56	38	93–61	260 ± 1	6.9 × 10 ¹³
BACY/BMP/CPM	400	460	69	52	—	—	—

T_i = initiation temperature, Tlend = temperature at the end of first stage decomposition.

^a Corresponds to the initial part of the first stage decomposition for the blends and entire part of major decomposition for the homopolymers.

improvement in the mechanical characteristics of the latter. However, their role as a network interlinker in B–T systems has not been described. While its effect on the mechanical performance of the blends remains to be described in an ensuing publication, *p*-CPM did not alter the initial thermal decomposition temperature of the blend containing them. However, the interlinker reduced the rate of degradation at higher temperature, leaving significant char residue. The TGA thermogram for one such linked blend is included in Figure 9.

Thermal Decomposition Kinetics

The kinetics of thermal decomposition of the homopolymers and the blends were analyzed by the Coats–Redfern equation as described above. For calculating the fractional decomposition (α), the mass loss at 700°C was considered as 100% decomposition for the purpose of uniformity in all cases. Only the major decomposition step evident in the thermogram was considered for analysis. The mass-loss range of the degradation step considered for the calculation is given in Table I. Since the polymer undergoes random decomposition, first-order kinetics was assigned without serious error. The kinetic parameters were calculated by plotting $\ln(g\alpha)$ versus $1/T$ as per eq. (2) as shown in Figure 10 in typical cases. While the polycyanurate underwent degradation in an apparently single step, kinetic analysis revealed a two-stage mechanism for the bismaleimide for the major step, although TGA revealed an apparent single-step degradation. The kinetic parameters for the two steps were independently calculated

for this polymer. The low activation energy for the second step implies an easy volatilization process. In case of the blends, the kinetic plot was linear only for the initial 10–15% mass loss. Beyond this, interference from the mass loss arising from the bismaleimide made the linear regression imperfect and, hence, only the initial degradation was considered in these cases. It may be noted that the activation energy calculated for the initial decomposition of the blends corresponds (within experimental error) to the values for the pure polycyanurate, confirming that the initial decomposition of the blend is caused by the polycyanurate component.

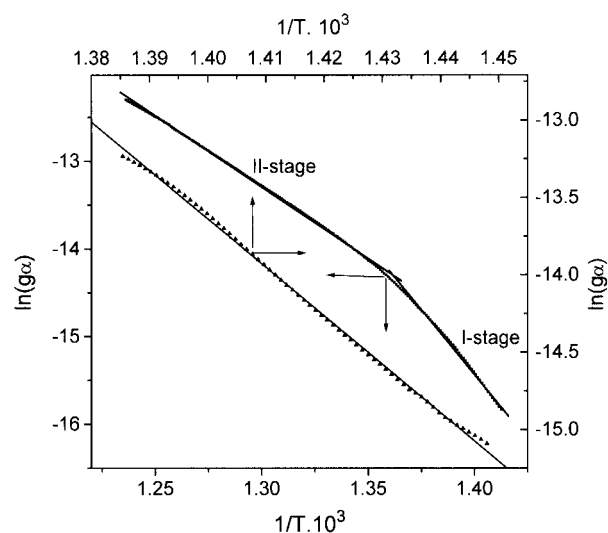


Figure 10 Determination of kinetic parameters for thermal decomposition: (■) poly(BMP); (▲) poly(BACY).

CONCLUSIONS

In the presence of DBTDL as a catalyst, the BACY-BMP blend underwent sequential polymerization, each component polymerizing independent of the other. The evidence for the sequential polymerization was obtained from both DSC and DMA analyses. The kinetics of the nonisothermal cure of the bismaleimide component helped predict its cure profile under actual polymerization conditions which was substantiated by isothermal DMA studies, both leading to optimization of the cure conditions. The cured polymer blends were found to undergo two-stage decomposition, each stage corresponding to the component of the blend. While the initial decomposition temperature was unaffected, increasing the bismaleimide retarded the rate of thermal erosion of the blend at higher temperature. The high-temperature stability was substantially improved on incorporation of a potential network interlinker containing both maleimide and cyanate functions. The kinetics of nonisothermal degradation of the polymers for the major step of decomposition confirmed that the initial decomposition of the cured blends corresponds to the polycyanurate component. The physical, mechanical, and dynamic mechanical characteristics and morphological features of the blends, their application in laminate composites, and the dependencies of these properties on blend composition are the subjects of an ensuing publication.²³

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