

Effect of Polymeric Additives on Properties of Glass–Bisphenol A Dicyanate Laminate Composites

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ABSTRACT: The polycyanurate network matrix derived from the thermal, dibutyl tin dilaurate catalyzed polymerization of bisphenol A dicyanate was modified in their glass–laminate composites with different linear polymeric additives bearing pendant phenol, cyanate, and epoxy functions. The mechanical properties and fracture energy for delamination of the glass–laminate composites were estimated as functions of the backbone structure and concentration of the various additives. The effect of altering the nature or concentration of the functional group for a given backbone structure of the additive was examined in some cases. Except for the epoxy functional acrylic polymer, all other systems adversely affected the fracture energy for delamination of the composites due to either plasticization or embrittlement of the matrix. With the exception of the styrene-hydroxyphenyl maleimide (SPM) copolymer, the other modifiers impaired the mechanical properties and adversely affected the thermomechanical profile of the composites. In the cases of the phenol functional acrylic polymer and its cyanate derivative, plasticization of the matrix by the partly phase-separated additive, which eased the fiber debonding, appears to be responsible for the impairment of the mechanical properties. The high glass transition temperature SPM copolymer enhanced the resin–reinforcement interaction through dipolar interactions induced by the hydroxyl groups, which resulted in amelioration of the mechanical properties. However, its possible coreaction and formation of a brittle, homogeneous phase with the polycyanurate was conducive for poor damage tolerance. The SEM analysis of the fractured composites showed that in the elastomers fiber debonding is the major cause for delamination. Although the presence of SPM led to a stronger interphase, failure occurred either in the brittle matrix or through fiber breakage. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 75–88, 2000

Key words: bisphenol A dicyanate; polycyanurate; composite matrix modification; laminate composites; cyanate-functional acrylic copolymer; styrene-hydroxyphenyl maleimide copolymer; fracture energy for delamination

INTRODUCTION

Advanced composites based on matrices like epoxy and bismaleimides in combination with reinforcements like glass, graphite, and so forth, are generally brittle, resulting in poor damage toler-

ance. Unlike these thermosets, cyanate esters and phenolic-triazine resins possess built in toughness due to the flexible ether linkages in the network. However, the bulky triazine rings in the crosslinked network restrict the rotations in the backbone to some extent, with the result that the toughness of the system is inferior to that of high temperature resistant thermoplastics. In order to enhance the fracture toughness of advanced composites, approaches based on a rubber-toughened

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matrix¹ and blending with tough and high temperature resistant thermoplastics like poly(ether ether ketone), poly(ether sulfone), and poly(ether imide) are generally being adopted.^{2–6} The addition of reactively terminated engineering thermoplastics is another accepted practice for improving the impact resistance.^{7–9} Modification by systems bearing reactive functions like hydroxyl and cyanate is of particular interest because they were found to enhance the toughness and impart solvent resistance by providing high interfacial adhesion without seriously affecting the glass transition temperature (T_g) or modulus.¹⁰ Telechelics modified with propargyl and vinyl benzyl end caps,¹¹ cyanate-terminated poly(aryl ether sulfone) and polysulfone,¹² blends with thermoplastic polyimides and siloxane polymers,^{13–15} and so forth, are known to improve the impact resistance of cyanate esters and their composites.

Several studies focused on the impact of matrix modifiers on the mechanical performance of neat resins and its translation to their composites. As a general rule, the modifications brought out in the mechanical properties of the neat resin are hardly translated on a one to one basis to the composites. This arises from the fact that the failure mechanisms in neat resins and composites are different. Therefore, it is not imperative to study the property variations in a neat resin to understand or predict the behavior in a composite.

The majority of the applications of cyanate esters, in particular of bisphenol A dicyanate (BACY), is in the form of composites. There have been many reports on the properties of composites based on BACY. However, almost all of them miss the key information on details of the processing of the composite because they are mostly patented. The objectives of the present work were to optimize the process for laminate composites of BACY with glass reinforcement and to investigate the effect of certain newly synthesized, high molecular weight polymers (of different backbones bearing varying pendant functional groups) on their mechanical properties. For reasons stated above, the polymeric additives were examined for their impact on the mechanical properties of composites rather than on the neat resins. This article describes the synthesis of these additives and the studies on laminate composites based on their blends with BACY, the process optimization of which forms another objective of the study. The trends in mechanical, dynamic mechanical, and fracture properties were examined as functions of

the backbone structure, nature, and concentration of the additives and correlated to the possible matrix morphology and the resin–reinforcement interaction. The dependence of these properties on the nature of the functional group and their concentration for the same backbone structure was also examined in limited cases.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, CDH, India), acrylonitrile (AN, CDH), styrene (Alpha Biochem), and butyl acrylate (BuA, E. Merck, Germany) were purified by passing through an alumina column, after ensuring the absence of polymer. Glycidyl methacrylate (GMA, E. Merck) was purified by vacuum distillation. Azobisisobutyronitrile (AIBN, Ajax Chemicals Laboratory, India) was recrystallized from methanol. Cyanogen bromide (CNBr, CDH) was purified by sublimation and triethyl amine (SD Fine Chemicals, India) was distilled from CaH₂. The BACY was synthesized by a known procedure.¹⁶ *N*-(4-hydroxyphenyl) Maleimide (HPM) was also synthesized by a reported procedure.¹⁷ Synthesis of terpolymers of styrene, HPM, and *N*-phenyl maleimide of different compositions (SPM-I, SPM-4) are described elsewhere.¹⁸ Dimethyl formamide (DMF, SD Fine Chemicals) was distilled from P₂O₅, methyl ethyl ketone (MEK) was distilled from K₂CO₃, and THF was distilled from CaH₂ (Nice Chemicals, India). Methanol (Ranbaxy, India) and dibutyl tin dilaurate (DBTDL, E. Merck) were used as received. Plain weave, silane treated E-glass fabric with a thickness of 0.25 mm (Unnathi Corporation, India) was used without any surface treatments.

Instruments

FTIR spectra were recorded with a Nicolet 510 P instrument. The cure characteristics of the resins were studied by DSC using a Mettler TA 3000 system at a heating rate of 10°C/min in static air. NMR spectra were recorded with a Jeol FX 90Q 90-MHz spectrometer. Gel permeation chromatography (GPC) analysis was performed on a Waters GPC model Delt. Prep. 3000 using THF as the eluent and with DRI-R 401 refractive index and UV (at 254 nm) detectors. Elemental analyses were performed using a Perkin–Elmer model 2400 elemental analyzer. Dynamic mechanical

Table I Characteristics Polymeric Modifiers

Polymer	Functional Group	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	Equiv Weight	Remarks
EPOBAN	Epoxy	10.4	5.5	1.8	5320	Epoxy elastomer
BNM	Phenol	4.3	1.8	2.3	1890	Phenol functional elastomer
BNMC	Cyanate	8.8	2.0	4.4	1890	Cyanate elastomer, backbone similar to BNM
SPM-1	Phenol	10.8	3.3	3.2	940	Phenol functional high T_g polymer
SPM-2	Phenol	10.1	5.3	1.9	300	Differ from SPM-1 only in phenol concn

analysis (DMA) was carried out with a Du Pont DMA-983 at a frequency of 1 Hz. Single ply prepreg was used for DMA analysis of the resin and for composites; $60 \times 12 \times 2$ mm³ specimens were used.

Synthesis of Polymeric Additives

BuA-AN-HPM Terpolymer (BNM)

The phenol-functional terpolymer (BNM) was realized by the free radical copolymerization of BuA, AN, and HPM (60:30:10% by weight) in DMF solution in the presence of AIBN (0.1 wt %) as the initiator. The reaction was carried out at 70°C for 8 h in sealed, evacuated flasks after the usual freezing, evacuation, and thawing. The polymer was precipitated into a 9:1 methanol-water system, purified by repeated precipitation from the acetone solution, and dried at 70°C for 5 h. The yield was 55%. The polymer was characterized by elemental analysis and proton NMR.

Cyanate-Functional Terpolymer (BNMC)

BNMC terpolymer was synthesized from BNM precursor by a reaction with CNBr at -30°C in the presence of triethylamine. In a typical experiment the BNM (20 g, phenol equiv wt = 1890) was dissolved in 100 mL of THF and triethylamine (2.68 g, 0.0264 mol) was added to it. The product was added dropwise into 2.80 g of CNBr (0.264 mol) dissolved in 200 mL of THF in a three-necked RB flask. The triethylamine hydrobromide was filtered off and the BNMC was isolated by precipitation of the filtrate into a 9:1 methanol-water mixture. The filtered product was dried in air and was kept as a 10% solution in MEK at 0°C. The yield was 71%. The polymer required for characterization was isolated by evaporation of the solvent under a vacuum at

room temperature, and it was characterized by FTIR and GPC.

Styrene-Hydroxyphenyl Maleimide-Phenyl Maleimide Terpolymer (SPM)

Two types of terpolymer of different compositions (SPM-1 and SPM-2) were synthesized using an equimolar molar mixture of styrene and maleimide (phenyl maleimide and HPM together) in DMF using AIBN as the initiator. Details are described elsewhere.¹⁸

Epoxy-Functional Acrylic Copolymer (EPOBAN)

The EPOBAN copolymer was realized by the free radical copolymerization of BuA, AN, MMA, and GMA. Its preparation is the subject of an Indian patent application.¹⁹ The molecular characteristics of the copolymer are compiled in Table I.

Characterization

The various functionalized polymers were characterized by FTIR, ¹H-NMR, GPC, and DSC.

Synthesis of Prepreggable-Grade BACY

The BACY resin required for prepregging was prepared by solution polymerization of BACY in MEK. Thus, 50 g of BACY dissolved in 50 mL of MEK containing 50 mg DBTDL was heated in an oil bath at 90°C for 8 h. The resulting viscous solution was used as such for prepregging.

General Method for Preparation of Blends of BACY with Additives

The BACY oligomer solution prepared as above was mixed with MEK solutions of the various additives in required quantities (5, 10, 15, and

20% by weight of BACY). These solutions were directly used for prepregging with the E-glass fabric.

Preparation of Laminate Composites

Glass fabric reinforced laminates (40 plies, 12 × 10 cm) of BACY and its blends with SPM, EPOBAN, BNM, and BNMC additives at different concentration levels were prepared by solution dipping of the fabric followed by drying for 18 h at room temperature. The plies were cut and stacked between two metallic sheets and dried in a vacuum for 2 h at room temperature to remove any entrapped solvent. A thin layer of Teflon-coated fabric was kept between the metal and prepreg to prevent adhesion of the resin to the metal. Prior to heating, a pressure of 50 kg/cm² was applied for 5 min for initial compaction of the plies. After this compaction the pressure was released and the platens were heated with the prepreg under contact pressure. At the point of gelation of the resin, a pressure of 27.5 kg/cm² was applied and this pressure was maintained throughout the process. The time-temperature schedule for the cure process of the composites is as follows: the temperatures were 90, 150, 200, and 25°C for 45, 30, 30, and 30 min of heating time, respectively.

Determination of Fracture Energy for Delamination

The interlaminar fracture energy of the laminates was determined by the end-notch flexural method according to ASTM D 30.02. An initial crack length of 25.4 mm was given at the end of the middle plane of the 24 ply laminate, which had dimensions of 100 × 10 × 5 mm³.

Determination of Resin Content and Sol-Gel Content of Composites

The sol content was determined by monitoring the mass loss of the weighed specimens subjected to Soxhlet extraction using MEK for 72 h. The resin content in the composite was determined from the mass loss by air oxidation of the specimens at 800°C for 4 h. In general, the resin content was maintained in the range of 27–30% by weight.

Mechanical Testing

Mechanical testing of the laminates was performed according to the ASTM specifications as detailed below:

1. ASTM D 790 for flexural strength,
2. ASTM D 30.02 for fracture energy,
3. ASTM D 3410 for 0° compressive strength, and
4. ASTM D 2344 for interlaminar shear strength (ILSS).

The test specimens were machined from the cured laminates and tested in accordance with the above ASTM testing standards using an Instron Universal Testing Machine (model 4202).

Fracture Analysis of Neat Resins and Laminates

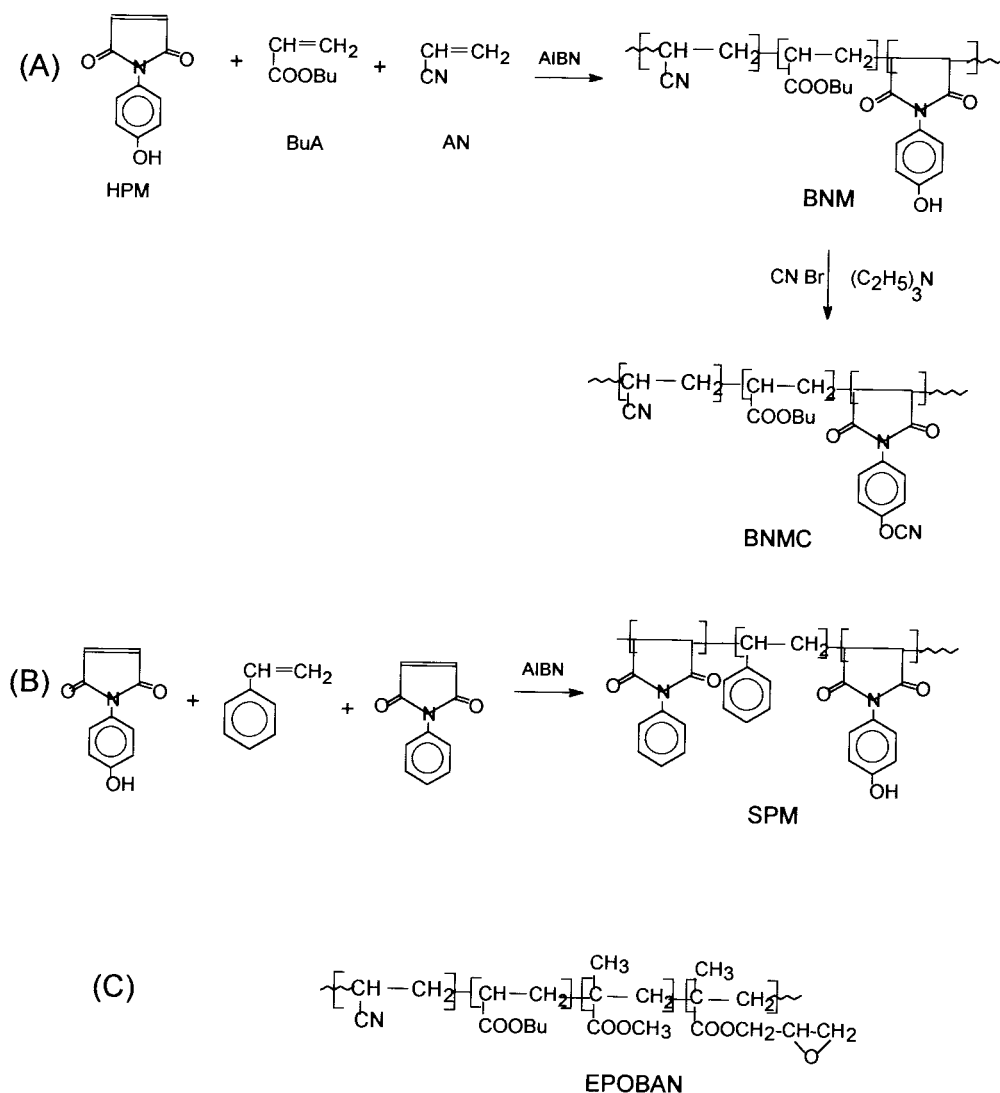
The fractured surfaces of neat resins and composites were subjected to SEM analysis. A conductive layer of gold was coated over the fractured surface by the plasma vapor deposition technique and was viewed with a Stereoscan MK 250 Microscope (Cambridge Instruments).

RESULTS AND DISCUSSION

Synthesis and Characterization of Additives

Linear polymers of different backbones with pendant phenol, cyanate, and epoxy functions, which could serve as modifiers for the BACY matrix in its composites, were synthesized. The epoxy-functional EPOBAN and phenol-functional BNM polymers were made by the free radical copolymerization of appropriate monomers. The synthesis of BNM is represented by Scheme 1 whereas that of EPOBAN is covered in a patent.¹⁹ They were characterized by GPC, FTIR, ¹H-NMR, and TGA. The ¹H-NMR of BNM showed that the copolymer contained BuA, AN, and HPM in the ratio of 6.2:3.2:1 by weight. EPOBAN contained BuA and AN in the weight ratio 7:3 and possessed an epoxy content of 0.2 equiv/kg. The synthesis of the SPM series was described earlier.¹⁸ Their structures are included in Scheme 1. It may be noted that the backbone structures of BNM and BNMC are the same, but they differ in the nature of the pendant groups. Similarly, the SPM series has the same backbone but differs in phenol content as given in Table I.

The cyanate-functional terpolymer BNMC was synthesized from BNM by its reaction with CNBr as shown in Scheme 1. This terpolymer was characterized by GPC, FTIR, and DSC. In the FTIR the absorptions due to cyanate groups appeared at 2270 and 2240 cm⁻¹ at the cost of the peak at



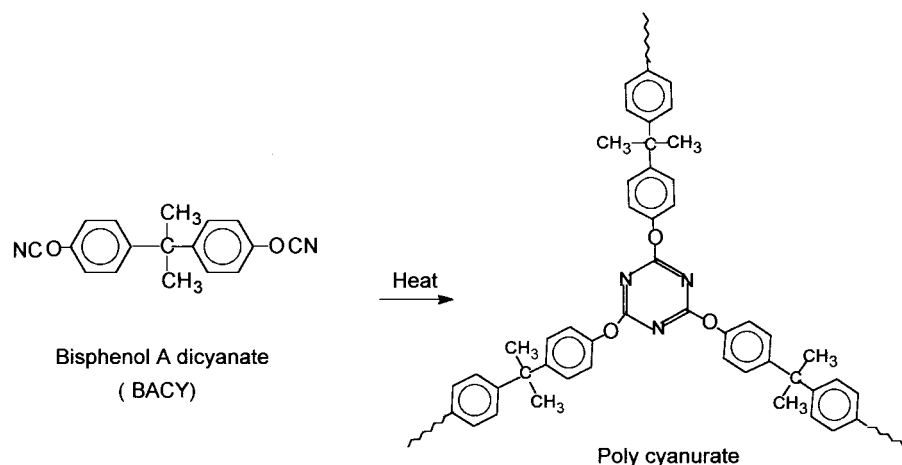
Scheme 1 (A) The synthesis of phenol-functional terpolymer (BNM) and its cyanate-functional derivative (BNMC), (B) the synthesis of SPM copolymer, and (C) the structure of EPOBAN.

3400 cm^{-1} that was due to the phenolic-OH of BNM, indicating the complete conversion of phenol to cyanate. Table I gives the characteristics of the synthesized polymeric modifiers. The GPC analysis showed that on cyanation of BNM, the molecular weight of the derivative increased marginally. The DSC analysis of BNMC exhibited a single cure exotherm at around 250°C , which was due to curing through the cyanate groups. It may be noted that BNM and BNMC possess the same backbone but differ in the nature of the pendant groups. In this work these additives were blended with partially polymerized BACY and their influence on mechanical, thermomechanical, and frac-

ture behavior of the resulting composites was analyzed. BACY polymerizes to the polycyanurate network as shown in Scheme 2.

Resinification (Partial Polymerization) of BACY

Partially polymerized BACY resin was found to possess the good tackiness required of a resin for composite fabrication. Moreover, the partial polymerization can avoid the rapid thermal polymerization when the pure monomer is directly polymerized. Because bulk polymerization of BACY at times gets out of control because of the high exothermicity, the resinification was done in MEK at



Scheme 2 The formation of a polycyanurate network from BACY.

90°C in the presence of 0.1 wt % of DBTDL as the catalyst. The extent of cyanate conversion (α) with time was monitored by DSC from the residual enthalpy of polymerization of the resin isolated at different time intervals. It was calculated by the relation, $\alpha = 1 - (\Delta H_t / \Delta H_0)$, where ΔH_t is the enthalpy of polymerization of the resin isolated at time t and ΔH_0 that of the pure monomer.

The time–conversion profile is shown in Figure 1. The reaction was continued for 8 h when 30% of the cyanate underwent curing and the resultant resin possessed good tackiness. The solution with a bulk viscosity of about 100 cps was used as such

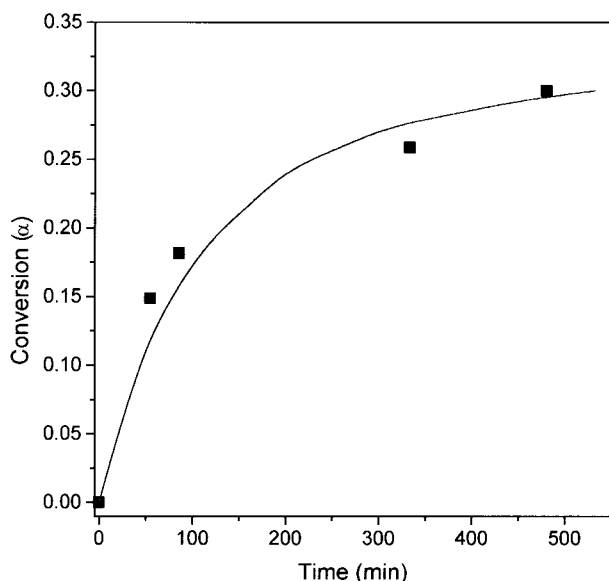


Figure 1 A time–conversion plot for the solution polymerization of BACY at 90°C.

for impregnation. From the mean field theory the average molecular weight of the resin was estimated as 1110. The GPC analysis of the products isolated at different time intervals revealed the presence of a broad distribution of oligomers of varying molecular weights in the resin; the higher molecular weight fraction increased with conversion. The GPC traces are shown in Figure 2. The relative amount of unreacted monomer (BACY) was calculated by the manual deconvolution of the GPC profile, which amounted to 30.5% at a cyanate conversion of 30%.

Cure Characterization of Resin and Prepreg

The DSC, FTIR, and DMA (isothermal and dynamic) techniques were employed to optimize the processing of the composites. The DSC studies on BACY carried out in the presence of 0.1% by weight of DBTDL revealed the onset of cure at $\sim 110^\circ\text{C}$.²⁰ The DMA of the prepreg was also carried out to study the viscoelastic changes occurring during curing of the prepreps. The DMA under dynamic heating is shown in Figure 3. The initial decrease in storage modulus (E') at around 75–80°C is associated with the softening of the resin. This was followed by a sharp rise in E' at 150°C, indicating gelation. The $\tan \delta$ curve exhibited a minimum at gelation occurring at this temperature. After the rigidification a further increase in the temperature resulted in a diminution of E' due to softening of the cured resin.

At the point of gelation, a pressure of 27.5 kg/cm² was applied for compaction of the plies during the composite fabrication. Figure 4 shows the DMA spectrum of the prepreg that was heated

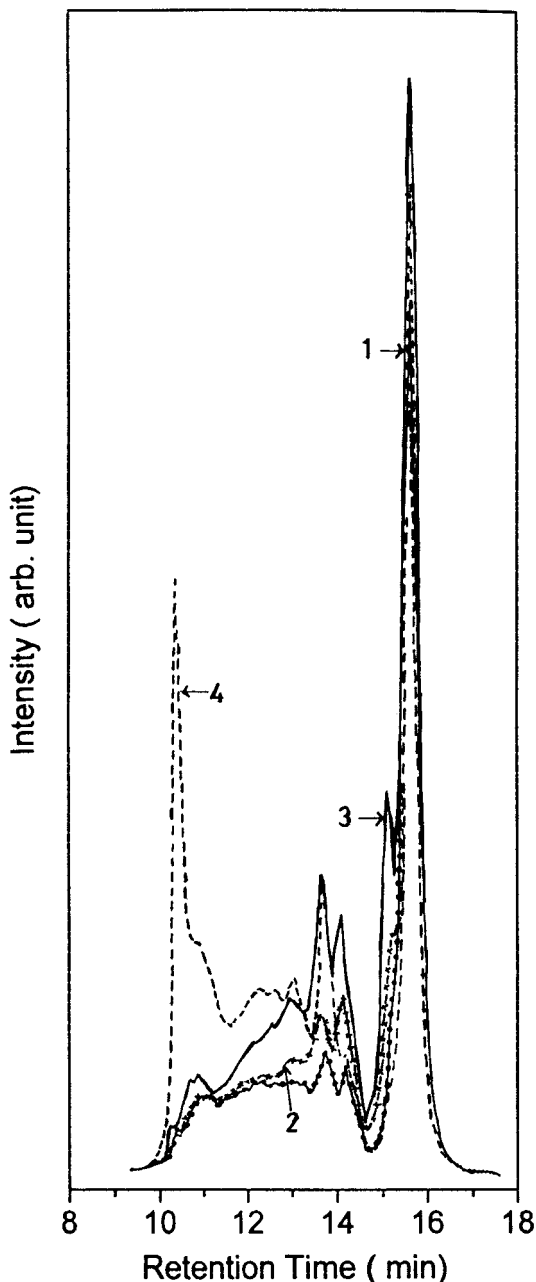


Figure 2 GPC profiles of the partially polymerized BACY at different time intervals: (●) 1 for 35 min; (×) 2 for 95 min; (—) 3 for 215 min; (- - -) 4 for 480 min.

to 250°C under dynamic heating followed by isothermal heating at 250°C. Isothermal DMA of the prepreg suggested postcuring for about 30 min at 250°C, because after 30 min the η^* and E' values both became practically steady. The cure profile of the prepreps was not altered significantly by the presence of the polymeric additives, because the strong catalysis by DBTDL outweighs the effect of

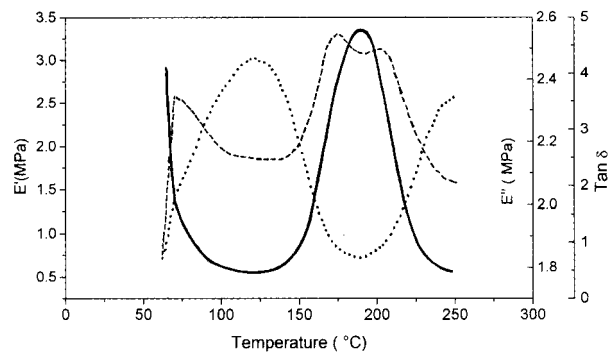


Figure 3 The DMA of BACY-glass fabric (prepreg): (—) E' , (- - -) E'' , and (· · ·) $\tan \delta$. The heating rate is 2°C/min.

other functional groups on the cure of BACY. The composites were heat cured in stages under the heating schedule given in the Experimental section.

Effect of Polymeric Additives on Mechanical Properties of Glass-Laminate Composites

EPOBAN

Glass laminates were prepared by varying the concentration of EPOBAN from 5 to 20% by weight in the matrix. The mechanical properties and fracture toughness of glass-cyanate ester composites are reported to be superior to those of glass-epoxy laminates.²¹ Cyanate ester is known to coreact with epoxy groups^{6,22} to form poly(oxazolidinone) as the major product. However, it appears that in this particular system the glycidyl function does not readily coreact with the cyanate. This was evident from the Soxhlet ex-

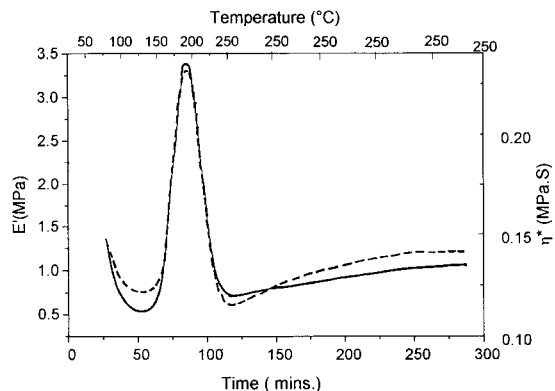


Figure 4 The isothermal DMA of BACY-glass (prepreg): (- - -) E' and (—) η^* . The heating rate for the nonisothermal part is 2°C/min.

Table II Mechanical Properties of Glass Laminate Composite

Additive	Concn (wt % BACY)	Mechanical Properties					
		Flexural Strength (MPa)	0° Compress Strength (MPa)	ILSS (MPa)			Fracture Energy (kJ/m ²)
				Ambient	150°C	Retention at 150°C (%)	
NIL	0	544	295	58	38	66	2.60
EPOBAN	5	401	204	33	24	72	—
	10	503	212	54	31	57	—
	15	501	219	54	17	32	2.50
	20	507	166	40	15	37	2.64
	BNM	5	426	240	46	31	78
BNMC	10	610	220	59	23	39	—
	15	525	260	54	23	43	1.66
	20	420	227	54	24	44	—
	BNMC	10	521	257	56	25	45
SPM-1	15	533	262	49	15	31	1.56
	5	542	233	71	40	56	—
SPM-4	15	598	240	71	50	70	1.31
	15	550	215	73	41	56	1.30

traction of the composite that showed that only about 20% of the added polymer really entered the cyanurate network through coreaction while the rest remained as dispersed particles. The lack of coreaction led to a two-phase morphology that was also evident in the DMA of the cured laminates. The addition of EPOBAN resulted in a drastic reduction in ILSS that was due to intercalation of the elastomer at the interphase. The results given in Table II show that the presence of this elastomer causes a significant reduction in the high temperature ILSS values, particularly at higher concentrations. The compressive strength was lower at higher concentrations of EPOBAN because of plasticization of the matrix, facilitating the fiber dewetting. The compressive strength also showed a similar dependence on temperature. At a concentration of 10%, the property was retained to 69% whereas it was reduced to 47% at a 20% concentration of EPOBAN. The flexural strength, on the other hand, showed a sharp fall in the beginning and then tended to pick up when increasing the concentration of the additive. Under flexural load the specimen is subjected to transverse compression and longitudinal tension. It appears that the phase-separated elastomer promotes the longitudinal tensile strength, thus augmenting the flexural strength of the composite as a whole. At a lower concentration the elastomer is finely dispersed or solubilized in the ma-

trix, which causes considerable plasticization. This plasticization is responsible for the initial sharp fall in all mechanical properties (ILSS, flexural strength, and compressive strength). At higher concentrations the phase-separated elastomer confers toughness and restores the mechanical properties to a large extent. The solubilization of EPOBAN in BACY was evident from the decrease in the T_g of the BACY phase in the DMA.

The effect of the epoxy concentration on the properties was not investigated for this additive. This is because, EPOBAN has a unique combination of monomers that render it a tough, strong elastomer. Augmentation of the epoxy content requires incorporation of a monomer that would transform it to a high T_g polymer of different characteristics. In that case, a true comparison becomes difficult unless the effect of the backbone structure is also taken into account. However, it can be expected that on increasing the epoxy content, the possibility of coreaction with the cyanate increases and this may alter the morphology of the matrix and, consequently, the mechanical performance of the composites derived from it.

Phenol-Functional Acrylic-Maleimide Terpolymer (BNM)

It is known that inclusion of a rigid structural unit like maleimide brings about the enhance-

ment in T_g of acrylate backbones.²³ Incorporation of maleimide-based, high T_g polymers into brittle epoxy matrices was found to enhance the mechanical performance, particularly the fracture toughness of the latter.²⁴ BNM copolymer containing 0.05 mol % of HPM was incorporated in the cyanate matrix. This polymer has a comparatively low T_g and possesses flexibility and high cohesive strength. Phenol groups are known to participate in the cyclotrimerization of cyanates, replacing the less nucleophilic phenol in the triazine. However, maleimidophenol, which is less nucleophilic than bisphenol A (of BACY), is not expected to participate in the network formation. This was proven in the Soxhlet extraction of the cured matrix when BNM was completely extracted out. BNM forms a separate phase in BACY, especially at a higher concentration of it. Initially, the properties are lowered but are restored to a great extent at moderate concentration. The ILSS values are practically unaltered, while flexural strength and compressive strengths are adversely affected. The lowering in properties is less pronounced than in the EPOBAN, although a comparison between the two is not meaningful in view of their different backbone structures and concentration of the functional groups. BNM functions more or less the same way as EPOBAN in amending the matrix morphology and composite properties. At a given concentration, BNM performed better than EPOBAN. It can be seen that as in the case of EPOBAN, the ILSS retention at a higher temperature is less at higher concentrations of the additive, and the relative performance is also less than that of BNM. Thus, the ILSS was retained to 53% at 150°C for BNM (at 20% concentration) whereas it was only 47% for EPOBAN at the same concentration. This agrees with the comparative DMA results of the two cases. The DMA implied the existence of a separate plasticized phase containing part of the BNM dissolved in the BACY matrix unlike the case of the EPOBAN. Figure 5 shows the variation of the ILSS with the concentration of the additive. It also represents the relative retention of the ILSS at 150°C for different cases.

Cyanate-Functional Acrylic Terpolymer (BNMC)

When the phenol function of BNM was transformed to the cyanate (BNMC) and cocured with BACY, it coreacted with the dicyanate ester and became dispersed in the matrix as part of the network. The coreaction was confirmed from the

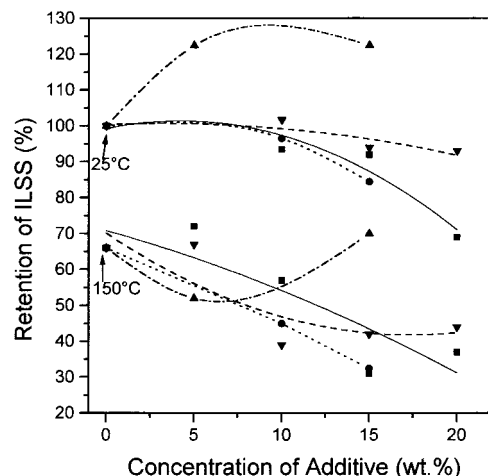


Figure 5 The variation of the ILSS of composites with a concentration of additives at room temperature and 150°C: (■ —) EPOBAN, (▼, - - -) BNM, (●, · · ·) BNMC, and (▲, - - - -) SPM-1.

IR spectrum of the cured compound that showed the absence of —OCN groups. Further, on Soxhlet extraction no soluble fraction was obtained unlike the case of the BNM. The addition of BNMC marginally decreased the composite mechanical properties, particularly the ILSS. Although the coreaction of BNMC facilitates its dispersion in the matrix, its flexible backbone could exert some plasticization effect, thus facilitating the resin debonding from reinforcement, as reflected by a decrease in the ILSS and related properties. The ILSS deteriorates sharply at high temperature, more than it does in the case of BNM or EPOBAN, as can be seen from Table II and their representation in Figure 5. This is due to the finer dispersion of part of the polymer additive as an integral part of the matrix. Thus, by retaining the elastomer nature of the backbone and replacing the weakly reactive phenol by the very reactive cyanate group, the properties of the composite were not improved, although the morphology was changed. On the other hand, the easy coreaction facilitated its finer dispersion that caused extensive matrix plasticization, resulting in poorer performance. The elastomeric BNMC might be rendering the matrix tougher, which remains to be investigated independently. As in the case of EPOBAN, the effect of the pendant group concentration on the efficacy of the matrix modifier was not studied because such polymers may not have comparable backbone structure and flexibility because these functional groups have to be incorpo-

rated through the phenyl maleimide vehicle that will progressively transform the elastomer to a rigid plastic. Thus, a true comparison becomes difficult.

Phenol-Functional Styrene-Maleimide Copolymers (SPM)

Phenol-functional terpolymers SPM-1 and SPM-4 with similar backbones but with different concentrations of phenol groups were examined as matrix modifiers for BACY. These polymers possess high a T_g .¹⁸ In these cases the glass-reinforced composites exhibited a clear enhancement in ILSS whereas the compressive and flexural strengths remained unaltered, as seen in Table II. Because the increased ILSS was not translated to the other properties, it is to be presumed that the failure takes place in the matrix, which was evidenced in the SEM analysis of the fractured surface. High temperature ILSS values (at 150°C) were also superior to that of pure BACY as can be seen from Figure 5. Soxhlet extraction in MEK gave a minimal amount of soluble fraction ($\approx 0.2\%$) for either case, implying coreaction of the additive with BACY, resulting in high T_g networks. As the concentration of the SPM-1 additive increases from 5 to 15%, all mechanical properties including the high temperature ILSS increase. Unlike BNM, these polymers contain a large proportion of hydroxyl groups, particularly SPM-2. It is enough that a few groups react with the BACY matrix in order to facilitate its miscibilization and uniform dispersion in the matrix, as evidenced also from the DMA studies. Enhancing the hydroxyl concentration did not affect the ILSS. However, it was detrimental for the flexural and compressive strength and the high temperature ILSS. Because the additive also forms part of the network, the enhanced fiber wetting can be expected to be promoted by the hydroxyl groups of the additive through enhanced polar interaction (including H bonding) with the glass surface. In fact, SPM type polymers are proven resin modifiers (for improvements in mechanical properties and fracture toughness) for epoxy systems²⁵⁻²⁷ and the same effect is also reflected here, although the studies were limited to only the composite. Thus, the SPM series of high T_g polymers leads to enhanced mechanical properties of the composites.

DMA of Composites

The composites were subjected to DMA analysis at a frequency of 1 Hz. In Figure 6 the percentage

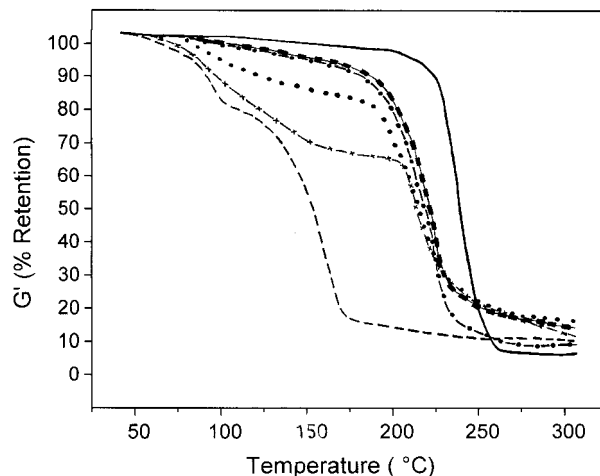


Figure 6 The DMA of BACY-based glass laminate composites: (—) BACY, (■) SPM-2, (●) SPM-1, (· · ·) BNM, (×) BNM, and (---) EPOBAN. The heating rate is 5°C/min.

retention of the room temperature storage modulus (E') is plotted as a function of temperature to normalize the anomalies resulting from differences in resin content for different systems. The EPOBAN-modified matrix exhibited two glass transitions at ~ 80 and $\sim 150^\circ\text{C}$, corresponding to the acrylate backbone of EPOBAN and the BACY network, respectively. A plateau region was observed in between the two transitions. The DSC of the composite also showed two transitions in this range, confirming that the EPOBAN-modified matrix exhibits a heterogeneous morphology in the laminate. EPOBAN is a low T_g polymer with a glass transition below room temperature ($\sim 10\text{--}15^\circ\text{C}$), and it has been observed that polycyanurate has a T_g of $\approx 250^\circ\text{C}$. However, the blend showed two T_g values in between these two extremes, implying that the two phases are not homogeneous by themselves. The first transition is caused by the elastomer phase containing part of the BACY dissolved in it and consequently with a higher T_g . Similarly, the BACY network contains some amount of EPOBAN dissolved in it, as a result of which the T_g of this phase is substantially lowered. Because no coreaction is expected, the matrix system can be considered as semi-interpenetrating polymer network. The overall lowering of the T_g is responsible for the poor high temperature retention of mechanical properties (ILSS and compressive strength) in this case. The plasticization of the matrix, especially at higher concentrations of the additive, is responsible for

easing the resin–reinforcement debonding, thereby diminishing the mechanical properties in general. The DMA of BNM- and BNMC-modified matrices also showed the presence of phase-separated morphology. Storage modulus curves showed two transitions corresponding to acrylate and triazine backbones occurring at around 90 and 200°C, respectively, as can be seen in Figure 6. The rubber phase is not pure and contains dissolved polycyanurate, and there is a consequent enhancement of the T_g from 40 to 90°C. The diminution in the T_g of the polycyanurate phase is marginal (by $\approx 30^\circ\text{C}$). The biphasic behavior and plasticization in the BNM was anticipated because the phenol groups are not present in an adequate concentration to enter into significant network linking with the cyanurate matrix. The cyanate-functional polymer (BNMC) completely coreacts with the continuous phase of the BACY. However, the cyanate functions are located statistically in the chain in small concentrations between segments of high molecular weight (≈ 5000 g/mol). This makes the elastomer segment between crosslinks form a separate phase. As a result of this, the cyanate-functional additive also exhibited a biphasic morphology with two glass transitions, one at around 90°C and another at $\sim 220^\circ\text{C}$, corresponding to the elastomer- and triazine-dominated phases. The low temperature transition is considerably less prominent when compared to its phenol counterpart and the major transition is that caused by the BACY matrix that does not experience a drastic fall in E' unlike the BNM. This is because BNMC is integrated into the matrix through chemical bonds. The partial plasticization by the elastomeric additives must be responsible for the low ILSS and poor compressive strength of the laminates in these cases.

In the SPM series of polymers, only a single transition was observed at around 225°C, which is marginally lower than that of pure BACY. It appears that the two phases are miscible, because otherwise a second transition due to pure BACY should have appeared at a higher temperature. The phenol concentration did not have any effect on the dynamic mechanical behavior. The uniform dispersion of the high T_g polymer and strong matrix–reinforcement interphase aided by the dispersed phenol functions must be conducive for the enhanced mechanical properties for this system. These polymers reportedly provide miscible blends with an epoxy matrix.^{25–27}

Fracture Energy for Delamination

In toughened matrices the impact strength depends on parameters like the nature of reactive functional groups, the curing agent, the concentration of the modifier, matrix ductility, particle size distribution, temperature, strain rate, and so forth. Previous studies showed that pendant functional elastomers impart significant improvements in fracture toughness to the neat resins, which is translated to the composites only to a limited extent however.^{28–30} In other words, the toughening effect of the resin is not proportionately transferred to the composite. The form of reinforcement, resin–reinforcement interaction, ply stacking sequence, fatigue properties, and so forth play a significant role in determining the toughness of laminate composites.^{31,32} Considerable improvement in the toughness of laminates could not be observed in the cases studied here. Such situations are known to arise when toughening mechanisms like crazing and shear banding and constriction of the plastic deformation zone in the matrix between reinforcements are absent.

In the case of reactive additives, effective molecular weight buildup by chain extension can enhance the ductility. This was expected for the EPOBAN. However, only a small portion (20%) of the epoxy functions of the polymer coreacted with the cyanate. The rest formed a separate phase, entangling some polycyanurate. This, together with the high molecular weight of the modifier, played a decisive role in determining the fracture energy of EPOBAN-modified composites. Thus, a slight enhancement in fracture energy was observed (by 40 J/m^2) at a concentration of 20% by weight of the additive, which was mostly due to the precipitated phase that prevents a crack and changes the direction of its propagation. Because the system exhibits good fracture properties, despite possessing a lower ILSS, it can be concluded that the fracture in this case propagated by the mixed mode (mode 1 and mode 2)

For BNMC-containing systems, blocking the reaction sites of BACY by the cyanate groups of the additives reduces the crosslink density of the modified networks. Although this might have enhanced the ductility of the system, fracture toughness was not improved. Most likely, the plasticization effect of the elastomer facilitated debonding from the fiber, reducing the fracture energy for delamination that takes place at the interphase mostly by mode 1 fracture (interlaminar). A

similar mechanism deteriorates the fracture energy of the BNM-modified composite. Thus, the fracture energies of BNM (1.66 kJ/m^2) and BNMC (1.56 kJ/m^2) are lower than those of unmodified BACY-based laminate (2.60 kJ/m^2) or EPOBAN-modified laminates (2.64 kJ/m^2). Table II includes the fracture energies of typical glass-reinforced laminates based on BACY.

Terpolymers similar to SPM with pendant phenol functions are known to improve the toughness of bismaleimides, epoxies, and so forth.^{25–27,33,34} The fracture toughness of the resins was reported to increase when the concentration of —OH groups of the additive were less than 3 mol %.³⁵ The SPM polymers envisaged here as matrix modifiers, however, possessed much higher concentrations of phenol functions in the chain (15–45 mol %). The phenol-functional polymer promoted a large interaction between the matrix–reinforcement, which resulted in a very strong interphase, as reflected in the values of the ILSS (Table II). The strong interphase was principally responsible for the improved mechanical performance in these cases. It is known that when the interphase is very strong, the whole composite can fail when the weakest fiber in the composite fails.³⁶ This appears to be the reason for the poor damage tolerance of SPM-modified laminates observed here. The embrittlement of the matrix leads to poor resistance to crack propagation of the matrix, thereby causing the mode 2 component of the failure mechanism to dominate in the system. Consequently, the fracture energies of the SPM-1 and SPM-2 containing systems were unexpectedly low at almost half (1.3 kJ/m^2) the value of the unmodified BACY-based glass laminate.

It appears that the BACY matrix has a unique network structure and morphology that offers op-

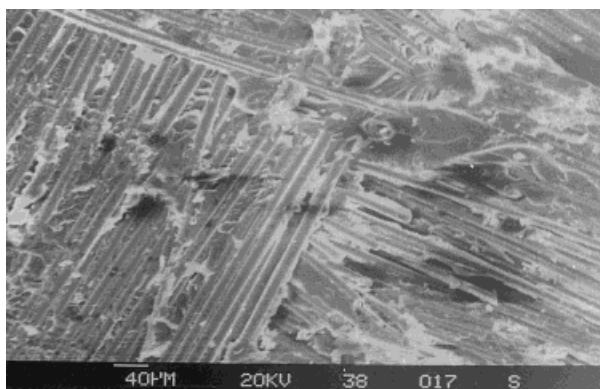


Figure 7 The SEM of glass–BACY laminate.

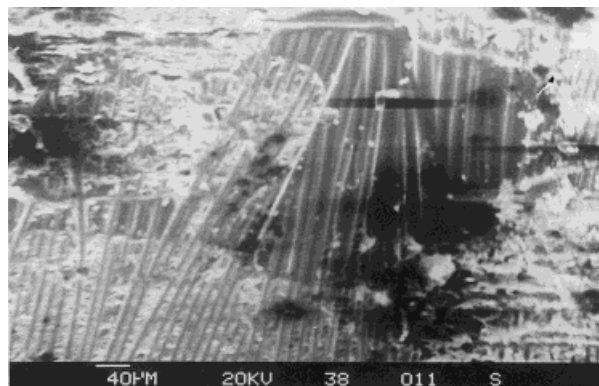


Figure 8 An SEM photograph of the EPOBAN-modified composite.

timum interaction with the glass reinforcement and that any conventional modifications aimed at matrix toughening or interphase fortifying has a detrimental effect on the damage tolerance of the composite.

Fracture Analysis of Neat Resins and Laminates

Fractured surfaces of the composites were subjected to SEM studies. Composites with a representative concentration of 15% by weight of the additive were chosen for SEM analysis in all cases. The SEM analysis of the fracture surfaces of the laminate suggests that the major fracture mechanism in unmodified BACY-based glass laminates is fiber breakage, as can be seen from Figure 7. Uniform wetting of the fiber surface could be seen, indicating a strong interphase in this case. In such cases the crack propagation path is known to be nonlinear and advances through transverse shear.³⁷ This mode of crack propagation requires higher energy compared to the delamination mode of failure usually observed in the case of laminates with a weak interphase. In the EPOBAN-containing composites the presence of large phase-separated domains could be conducive for enhancing the resin toughness (although it was not proven here), which is translated to the laminates only to a certain extent. Moderately good wetting of the fibers is seen in the SEM micrograph of the composite in Figure 8. The laminates in this case exhibited a mixed mode of failure involving delamination as well as matrix failure. The delamination may be caused at the locations where the well-dispersed additive causes plasticization and a weakened interphase. As a result, there is a marginal decrease in the ILSS and other properties of the composite. It

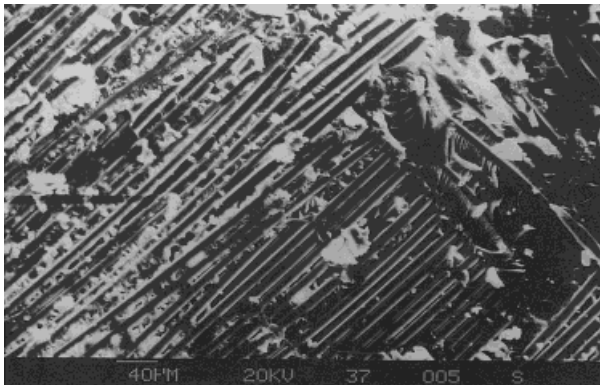


Figure 9 An SEM photograph of the BNM-modified composite.

appears from Figure 9 that fiber debonding is the major cause for the poor fracture energies in the composites with BNM added. BNMC-modified laminates also failed because of delamination similar to the BNM-containing systems, pointing to a weak interphase in both cases. As discussed earlier, the fine dispersion of BNMC causes a uniformly flexibilized matrix and uniformly debonded surfaces after fracture. Fiber breakage was practically not detected. The SEM photograph is shown in Figure 10 in this case.

SEM analysis of the SPM-containing laminates exhibited good wetting of the fiber. This is in conformation with the good ILSS, implying a strong interphase observed in this case. Therefore, as is evident from Figure 11 and as discussed earlier, the failure initiates in the matrix.

CONCLUSIONS

Prepolymerized BACY resin with good tackiness and drape could be obtained by its DBTDL-cata-

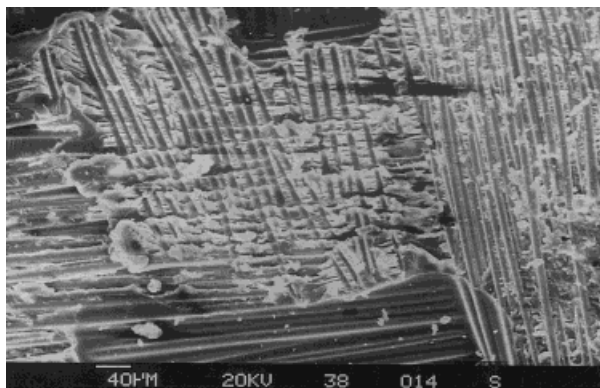


Figure 10 An SEM photograph of the BNMC-modified composite.

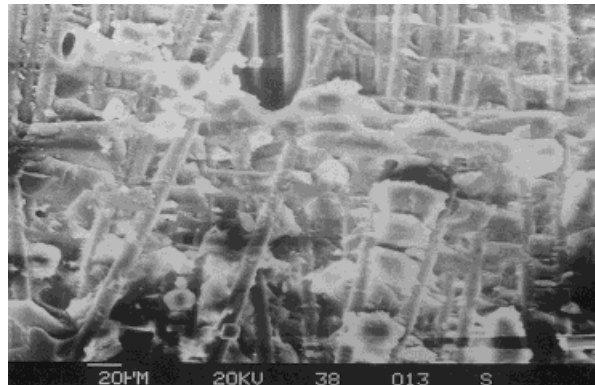


Figure 11 An SEM photograph of the SPM-modified composite.

lyzed solution polymerization. The polycyanurate network was modified in their glass laminate composites with different nonconventional polymeric additives bearing pendant phenol, cyanate, or epoxy functions but having a different backbone. The evolution in mechanical properties of the composites depended on the backbone structure of the additives and their concentration. Except for the epoxy-functional polymeric additive, all other systems adversely affected the fracture energy for delamination of the composites that was due to either plasticization or embrittlement of the matrix. Modification by polymeric additives is generally adverse to mechanical and thermo-mechanical characteristics. In the cases of the BNM and its cyanate, matrix plasticization by the partly phase-separated additive easing the fiber debonding was responsible for the impairment of the mechanical properties. The phenol-functional styrene-phenyl maleimide copolymer was found to ameliorate the mechanical properties of the composite at ambient conditions, although the high temperature properties were adversely affected. This high T_g polymer possibly enhanced the resin reinforcement interaction through dipolar interaction aided by the hydroxyl groups, but it was responsible for poor damage tolerance due to resin embrittlement. The available evidence points to the existence of homogeneous matrix morphology in this case. The possible expected improvement in resin toughness could not be proportionately transferred to the laminates. SEM analysis of the fractured composites lent support to the postulated mechanisms of failure in individual cases. Wherever a strong interphase was expected, failure occurred either in the matrix or through fiber breakage. Wherever the additives

caused plasticization, failure was caused by fiber dewetting. Replacing the phenol by cyanate for the same backbone led to finer dispersion of the latter in the matrix impairing the properties. This observation is in reference to the particular system studied here and cannot be generalized. Enhancing the phenol concentration for the strene-*alt*-phenyl maleimide polymer backbone deteriorated the flexural property because of matrix embrittlement. This study led to the conclusion that the BACY matrix by itself furnishes strong and tough composites and conventional resin toughening additives are generally not so effective in ameliorating the mechanical properties and damage tolerance of its composites.

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REFERENCES

- Uhlig, U. C.; Bauer, J.; Bauer, M. *Proc Macromol Symp* 1995, 93, 69.
- Krieger, R. B. 29th Int SAMPE Symp 1984, 29, 1574.
- Hirshbuehler, K. R. *SAMPE Q* 1985, 17, 46.
- Masters, J. E.; Courter, J. L.; Evans, R. E. 31st Int SAMPE Symp 1986, 31, 844.
- Yang, P. C.; Pickleman, D. M.; Wood, E. P. 35th Int SAMPE Symp 1990, 35, 1131.
- Pascault, J. P.; Galy, J.; Mechin, F. In *Chemistry and Technology of Cyanate Esters*; Hamerton, I., Ed.; Blackie: Glasgow, Scotland, 1994; p 112.
- Srinivasan, S. A.; McGrath, J. E. *Polymer* 1998, 39, 2415.
- Srinivasan, S. A.; Joardar, S. S.; Kranbeuhl, D.; Ward, T. C.; McGrath, J. E. *J Appl Polym Sci* 1997, 64, 179.
- Srinivasan, S. A.; Joardar, S. S.; Ward, T. C.; McGrath, J. E. *Polym Mater Sci Eng* 1993, 70, 93.
- Srinivasan, S. A.; McGrath, J. E. *High Perform Polym* 1993, 5, 259.
- Parker, D. G.; Wheatly, G. W. *Polym Int* 1994, 3, 321.
- McGrail, P. T.; Jenkins, S. D. *Polymer* 1993, 34, 677.
- Diberardino, M.; Pearson, R. *Int SAMPE Tech Conf* 1993, 25, 502.
- Lee, B. K.; Kim, S. C. *Polym Adv Technol* 1995, 6, 402.
- Pollack, S.; Fu, Z. *Polym Prepr Am Chem Soc Div Polym Chem* 1998, 39, 452.
- Grigat, E.; Putter, R. *Chem Ber* 1964, 97, 3012.
- Park, J. O.; Jang, S. H. *J Polym Sci Polym Chem* 1992, 30, 723.
- Mathew, D.; Reghunadhan Nair, C. P.; Ninan, K. N. *Eur Polym J*, to appear.
- Reghunadhan Nair, C. P.; Sivadasan, P. *Ind. Pat. Applic.* 451/MAS/99, April 1999.
- Mathew, D.; Reghunadhan Nair, C. P.; Krishnan, K.; Ninan, K. N. *J Polym Sci Polym Chem* 1999, 37, 1103.
- Patel, R. G.; Patel, V. S.; Patel, R. H. In *Polymer Science Recent Advances*; Bharadwaj, I. S., Ed.; Allied Publishers: New Delhi, 1995; Vol. 2, p 579.
- Grenier-Loustalot, M. F.; Lartigau, C. *J Polym Sci Polym Chem* 1997, 35, 3101.
- Chaudhary, V.; Mishra, A. *J Appl Polym Sci* 1996, 62, 707.
- Nield, E.; Rose, J. B. *U.S. Pat.* 3,652,726, 1972.
- Iijima, T.; Yoshioka, N.; Tomoi, M. *Eur Polym J* 1992, 28, 573.
- Iijima, T.; Ohnishi, K.; Fukuda, W.; Tomoi, M. *J Appl Polym Sci* 1997, 65, 1451.
- Iijima, T.; Hirano, M.; Tomoi, M. *Eur Polym J* 1993, 29, 1399.
- Iijima, T.; Suzuki, N.; Fukuda, W.; Tomoi, M. *Polym Int* 1995, 38, 343.
- Riew, C. K. In *Toughness and Brittleness of Plastics*, ACS Advances in Chemistry Series 154; Deanin, R. D., Ed.; American Chemical Society: Washington, D.C., 1976; p 326.
- Siebert, A. R. In *Proceeding of the 9th Discussion Conference on Macromolecules*, 1986.
- Scott, J. M.; Phillips, D. C. *J Mater Sci* 1975, 10, 551.
- O'Brien, T. K. In *Tough Composite Materials, Part II*; Volsteen, L. J., et al., Eds.; Noyes Publications: New York, 1985; p 14.
- Iijima, T.; Miura, S.; Fukuda, W.; Tomoi, M. *Eur Polym J* 1993, 29, 1103.
- Iijima, T.; Arai, N.; Takematsu, K.; Fukuda, W.; Tomoi, M. *Eur Polym J* 1992, 28, 1539.
- Iijima, T.; Suzuki, N.; Fukuda, W.; Tomoi, M. *Eur Polym J* 1995, 31, 775.
- Iijima, T.; Miura, S.; Fukuda, W.; Tomoi, M. *J Appl Polym Sci* 1995, 57, 819.
- Diefendorf, R. J. In *Tough Composite Materials, Part II*; Volsteen, L. J., et al., Eds.; Noyes Publications: New York, 1985; p 192.