Bisphenol A Dicyanate–Novolac Epoxy Blend: Cure Characteristics, Physical and Mechanical Properties, and Application in Composites

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ABSTRACT: Reactive blends of bisphenol A dicyanate (BACY) and a novolac epoxy resin (EPN) were investigated for their cure behavior and the mechanical, thermal, and physical properties of the cocured neat resin and glass-laminate composites. Contrary to the apparent observation in DSC, the dynamic mechanical analysis confirmed a multistep cure reaction of the blend, in league with an established reaction path for similar systems. The cured matrix was found to contain both polycyanurate and oxazolidinone networks that existed in discrete phases exhibiting independent glass transitions in dynamic mechanical analysis (DMA). The flexible and less crosslinked oxazolidinone network contributed to enhanced flexural strength at the cost of the tensile strength of the neat resin. The increased resin flexibility was, however, not translated to the glass-laminate composite for which the flexural strength decreased with the oxazolidinone content, although the latter was conducive for rendering a stronger interphase. The presence of oxazolidinone adversely affected the thermal stability of the cured resin and the high-temperature performance of both neat resin and the composites. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1675–1685, 1999

Key words: bisphenol A dicyanate; novolac epoxy resin; reactive blend; cyanate–epoxy blend; oxazolidinone polymer; polycyanurate; laminate composite

INTRODUCTION

Cyanate esters encompass several attractive physical, dielectric, thermal, and mechanical characteristics rendering them the material of choice in high-performance applications.[1–3] The dicyanate ester undergoes curing by cyclotrimerization to polycyanurate network with comparatively high glass transition temperature (T_g), low dielectric properties, low moisture absorption, good thermal stability, and excellent toughness for the matrix formed. These properties are tunable by proper choice of the backbone structure. Bisphenol A dicyanate (BACY) is a very versatile and ideal thermoset resin possessing most of the above properties and is capable of catering to many stringent requirements usually demanded in aerospace applications. However, the search to achieve further improvements in performance and reduction in cost is never ending and a variety of cocuring systems, selected on the basis of the cyanate ester chemistry, were attempted in recent years. Examples of cocuring systems are polyphenols, polyamines, anhydrides, bismaleimides (BMI), etc.[4] Among them, BMI and epoxies have evinced special interest. Cocuring of the blend of BMI and cyanate ester is now understood to lead to IPNs only,[5,6] and hence the interest in epoxy is revived owing to the reaction between epoxy and cyanate, giving rise mostly to oxazo-

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lidinone that can alter the matrix properties depending on the nature and composition of the blend. The CE/epoxy reaction was studied by many researchers. Blends of cyanate esters with bisphenol-based epoxy resins find increasing application in spacecraft structures because of their very low outgassing and good dimensional stability.[7] In recent studies, cyanate–epoxy coreaction and the reaction mechanism were investigated.[8–10] Most of the published literature on CE/epoxy systems refer to their reaction mechanism, kinetics, cure behavior, and thermal stability.[8–11] Information concerning the mechanical properties of neat resin and their composites remains patented. It is generally expected that coreaction between the two gives rise to new chemical structures, and consequently, the prediction of properties of the blend becomes difficult because they do not go by the rule of mixtures. Many multifunctional formulations, principally based on CE/epoxy, were claimed. Most of their applications are in copper-clad laminates,[12–14] fire-resistant formulations,[15] semiconductor devices,[16,17] etc.

In a majority of the reported studies, the epoxy resin used is bisphenol A based, which is characterized by inferior thermal characteristics.[11,18] The prospects for enhanced thermal stability for the resultant network increase by choosing a novolac-based epoxy such as EPN 1139. Several patent applications claim multicomponent systems containing BACY, novolac epoxy resin, and other reactants to have superior thermal stability than the conventionally cured bisphenol A-based epoxy or novolac–epoxy resin (EPN).[19] However, as in the case of cyanate esters, information on their blends with epoxy resins are also mostly patented.

This article concerns the reactive blending of EPN 1139 and BACY. The blends with different compositions were studied. The cure characterization and the mechanical, thermal, and physical properties of the cured neat resin blends and corresponding glass laminates are discussed. The article examines the composition dependency of these properties.

EXPERIMENTAL

Materials

BACY monomer was synthesized from bisphenol A (SD Fine Chem, India) and cyanogen bromide (CDH Chemicals, India) by a known procedure.[20] The epoxy resin, EPN 1139 (Ciba Geigy, Mumbai, India), with epoxy equivalent weight of 175 and epoxy functionality of 5.2/kg was used as received. Plain-weave, silane-treated E-glass fabric (Unnathi Corporation India; thickness = 0.25 mm) was used without any treatment. Methyl ethyl ketone (MEK, Qualigens, India) was distilled from K_2CO_3.

Instruments

FTIR spectra were recorded with a Nicolet 510 P instrument. The cure characteristics of the resins were studied by DSC by using a Mettler DSC-20 analyzer at a heating rate of 10°C/min in nitrogen atmosphere. Thermogravimetric analysis was performed on a DuPont 2000 thermal analyzer in conjunction with 951 thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10°C/min. Dynamic mechanical analysis (DMA) was performed using a DuPont DMA-983 in nitrogen atmosphere at a frequency of 1 Hz. Single-ply prepreg was used for DMA analysis of the prepreg and for composites, specimens of dimension $60 \times 12 \times 2$ mm^3 were used. Dielectric properties were determined by using an Inductance-Capacitance-Resistance (ICR) meter, Fluke PM 6306, at 25°C and 60% RH. Thermomechanical analysis (TMA) was performed with a Perkin–Elmer TMA 7 at a heating rate of 5°C/min.

Preparation of Cyanate Ester–Epoxy Blends (CEPOX)

CEPOX blends in varying proportions were prepared by melt-mixing BACY monomer with EPN 1139 (hereafter referred to as EPN) under vacuum. EPN was dissolved in molten BACY at 100°C, forming a homogeneous blend.

Determination of Gel Time of CEPOX Blends

Gelation of 1 : 1 equivalent mixture of BACY and EPN (CEPOX-1) was studied at 120, 130, 140, and 150°C. The gel time at 150°C was determined for various proportions of BACY and EPN. The following method was used. About 2 g of the homogenized blend was taken in a thin-walled glass tube and immersed in a thermostated oil bath at the required temperature. The resin was stirred with a glass thermometer, which also helps monitor the resin temperature. The time at which the resin ceases to flow and stick to the glass rod was taken as the gel time.

Table I Processing Schedule for CEPOX Laminates

Reference of Blend	Mol Fraction of Epoxy Groups	Duration of Precuring at 120°C (min)	Prepreg Processing Time (min)			
			100°C	150°C	200°C	250°C
CEPOX-1	0.50	105	30	20	30	60
CEPOX-2	0.40	135	30	45	30	60
CEPOX-3	0.30	165	30	60	30	60
CEPOX-4	0.20	195	30	90	30	60
BACY	0	[a]	30	90	30	60

[a] Resinified in MEK at 90°C for 8 h by using dibutyl tin dilaurate as catalyst.

Preparation of CEPOX Neat Resin Moldings

Neat resin moldings of the CEPOX blends and BACY were prepared by curing the molten resin in a rectangular aluminum mold after applying a silicone-mold release agent. Initially, the molten blend was deaerated under vacuum at 100°C. The temperature was slowly raised to 150°C and the blends were cured for 2 h. The formed slabs were taken out from the mold and postcured as per the following time–temperature schedule.

Temperature (°C)	150	200	250
Hold time (min)	30	30	120

The specimens were slowly cooled to the ambient temperature.

Preparation of CEPOX Laminates

By using the blend systems, glass fabric-reinforced composites (40 plies, 12 × 10 cm^2) were prepared. EPN readily dissolved in the molten BACY, forming a free-flowing solution. To make the resin prepreggable with good tackiness, the BACY–EPN mixture was prepolymerized at 120°C (in MEK, 55% by weight) prior to prepregging under the conditions described in Table I. This way, different compositions developed sufficient viscosity and tackiness for making prepregs. The conditions for prepregging and composite fabrication were selected on the basis of the composition of the blends, gel time, and cure temperature monitored by various experimental techniques. The prepregs were made by dipping the fabric in solution. They were dried for 18 h at room temperature, cut into pieces of the dimension 12 × 10 cm^2, stacked and molded in a hydraulic press between thick metallic platen to achieve a proper number of plies and thicknesses. The heating schedule is given in Table I. A pressure of 50 kg/cm^2 was applied for compaction of the plies immediately after the system attained 150°C for CEPOX-1 and -2. For CEPOX-3 and -4, the pressure was applied after 10 and 20 min, respectively, at this temperature because of their longer gelation time as given in Table I.

Mechanical Testing of Neat Resin and Composites

The test specimens of required dimensions were machined from the cured sheet (both for neat resin and composite) by using a diamond wheel cutter and tested in accordance with the following ASTM testing standards, by using an Instron Universal Testing Machine, Model 4202.

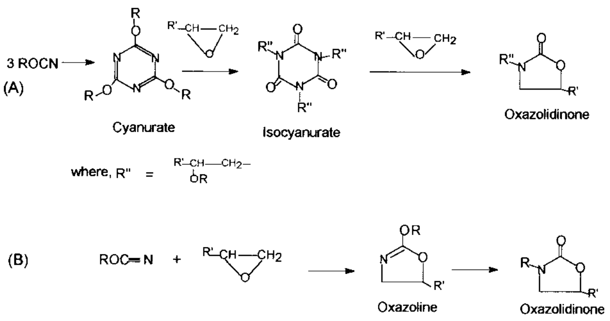
Tensile tests:	ASTM D638[21]	(neat resin molding)
Flexural strength:	ASTM D790[22]	(neat resin molding and composite)
0° Compressive strength:	ASTM D3410[23]	(composite)
Interlaminar shear strength (ILSS):	ASTM D2344[24]	(composite)

Resin Content

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

Determination of Moisture Absorptivity

Moisture absorption of the weighed specimens was determined by monitoring the weight gain after exposing the specimens to boiling water for 24 h. Rectangular specimens of an approximate dimension of 20 × 10 × 3 mm^3 were used for this.



Scheme 1 Cyanate–epoxy coreaction pathway.

RESULTS AND DISCUSSION

Cure Characterization

Cyanate esters are known to coreact with epoxy group to form oxazolidinone as the major product.[8–10,25–28] The reaction was shown to proceed through multiple steps involving the formation of intermediates like aryl cyanurate, isocyanurate, and oxazoline, as shown in Scheme 1. In the present study, BACY was cocured with EPN in varying proportions by keeping the cyanate ester/epoxy equivalent ratio always greater than one. The cyanate-rich systems were chosen to minimize the possibility of unreacted or homopolymerized epoxy groups in the cured system.

Figure 1 shows the FTIR spectra of CEPOX resin (CEPOX-1) prior to and after cure, showing the formation of oxazolidinone groups with absorption at 1750 cm^{-1}. A host of other groups with multiple absorptions in the region between 1650 and 1760 cm^{-1} also appear. These absorptions are caused by possible groups such as oxazoline[25], isocyanurate, cyanurate, etc., formed from the cyanate–epoxy reaction as was observed by other research groups.[8–10,29] In the complex cyanate–epoxy reaction, all these products are possible and no attempt was made to quantify their relative concentrations in the present study. The disappearance of cyanate absorption at 2270 and 2235 cm^{-1} and that of the epoxy groups at 915 cm^{-1} confirmed the total consumption of these groups during the reaction through one path or another. Strong absorptions due to the triazine rings at 1565 and 1365 cm^{-1} confirmed that an appreciable proportion of cyanate ester undergoes trimerization even at 1 : 1 cyanate/epoxy ratio, in league with the established reaction mechanism.[8,9,27,28] At higher concentrations of BACY, the triazine content in the system naturally increases.

DSC analysis of a 1 : 1 mixture of BACY and EPN (CEPOX-1) carried out immediately after mixing showed a single cure exotherm with cure initiation (T_i) at 160°C and a peak temperature of 246°C as shown in Figure 2. The reaction is ap-

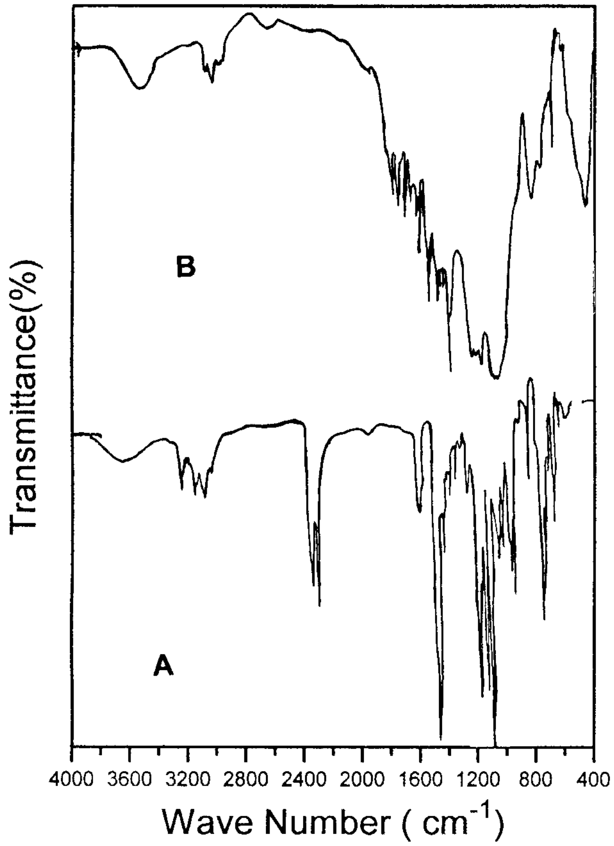


Figure 1 FTIR spectra of CEPOX-1. (A) Immediately after mixing, (B) after 2 h at 250°C.

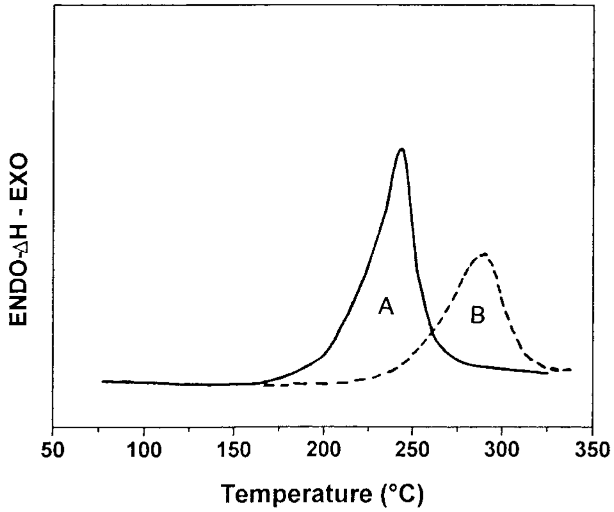


Figure 2 DSC trace of (A) CEPOX-1 immediately after mixing, (B) BACY.

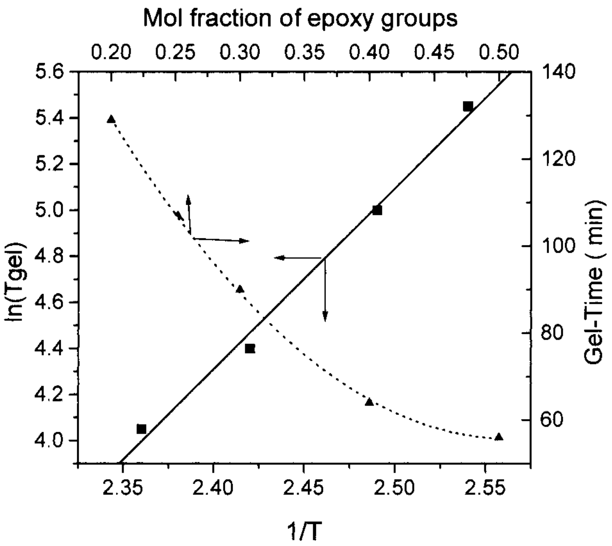


Figure 3 Dependence of gel time on temperature and composition.

parently complete at around 260°C with enthalpy of cure equal to 690 J/g. The curing of pure BACY (shown in the same figure) initiates at 208°C and the presence of epoxy functions was found conducive for decreasing the T_i by 48°C.

Gelation Behavior

Gelation is of great practical importance in the processing of thermoset resins because this key phenomenon, controlled by the processing conditions (temperature, pressure, time, etc.), has a direct bearing on the morphology and mechanical properties of the cured neat resins and composites. In the usual practice, thermoset formulations are heated in stages and preferably gelled at relatively lower temperature before postcuring them at a higher temperature. This is helpful in containing the likely high exothermicity of the reaction at higher temperature and also avoids the melt–flow of resins at higher temperature, particularly when the application of pressure is warranted, as in the case of composite fabrication. Gel time of the reactive blend is also dependent on their composition, presence of catalysts, and cure temperature. Thus, reaction of a cyanate ester/epoxy mixture in the presence 4,4′diamino diphenyl sulfone is reported to proceed faster than in its absence.[11] In the present CEPOX systems, no external catalyst was added and gel times (t_{gel}) were monitored at different molar ratios of the components and at different temperatures.

Figure 3 shows the dependence of composition and temperature on gel time. A linear relationship between ln t_{gel} and $1/T$ was observed for a 1 : 1 equivalent mixture (CEPOX-1). The gel time decreased with increasing concentration of the epoxy component. This is because epoxy groups promote the crosslinking through the multitude of reactions discussed above and can also catalyze the homopolymerization of BACY. Thus, CEPOX-1, which contained 1 : 1 equivalent mixture of cyanate and epoxy groups, manifested the lowest gel time. Bauer et al. established that up to the gel point, polycyclotrimerization of the cyanato groups is the dominating reaction.[30]

The cure reaction time and cure exotherms in the mold can be reduced considerably if the system is prepolymerized. Therefore, CEPOX mixtures were subjected to prepolymerization before molding the neat resin and laminate composites.

Neat Resin Moldings

Mechanical Properties

BACY-based polycyanurate and its composites are generally characterized by excellent mechanical properties and fracture toughness. In the present investigation, the mechanical properties of the cured blends were examined as a function of their composition. The results are compiled in Table II. The flexural strength of the resins increased with increasing EPN content, whereas tensile strength was found to decrease. The higher EPN content resin systems with possibly higher oxazolidinone content exhibited better resistance to bending stresses, whereas the increased concentration of these networking groups facilitated tensile elongation and an easy fracture. Thus, among CEPOX resins, CEPOX-1 possessed the maximum flexural strength and minimum tensile strength. The cured network contains both cyanurate (triazine) and oxazolidinone

Table II Mechanical Properties of BACY and CEPOX (neat) Resins

Resin	Flexural Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
CEPOX-1	114	33	15
CEPOX-2	99	24	—
CEPOX-3	95	25	18
CEPOX-4	—	37	14
BACY	90	70	11

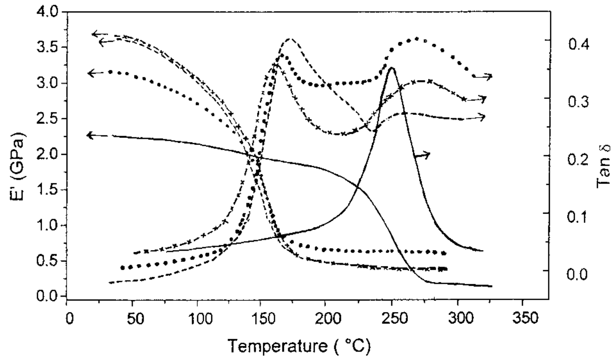


Figure 4 DMA of cured CEPOX (neat) resins. (- - -) CEPOX-1, (–×–×–×–×) CEPOX-3, (· · ·) CEPOX-4, (—) cured BACY.

rings. CEPOX-1 is expected to have maximum oxazolidinone composition. Quantitative formation of oxazolidinone in a 1 : 1 cyanate–epoxy mixture would have led to a thermoplastic polymer system. Insolubility of the cured resin confirms that the system contains other crosslinks such as cyanurates. Crosslink density increases as the cyanate content increases. Oxazolidinone ring constitutes a flexible structure with more thermoplastic character and thus accounts for the increased flexural strength and tensile elongation as the epoxy content increases in the blend. It can be concluded that these groups do not contribute to the cohesion as much as do the cyanurates (triazine); with the result, their presence decreases the tensile strength. Intermediate compositions like CEPOX-2 will have a dominant composite network structure, constituted by both oxazolidinone and cyanurates (triazine), showing intermediate mechanical properties.

Dynamic Mechanical Properties

Dynamic mechanical spectra of the cured blends showed substantial decrease in T_g in comparison to the pure polycyanurate. On increasing the cyanate content in the blend, the crosslink density increases because of the formation of a greater number of triazine rings, and this results in a systematic enhancement in both storage modulus (E') and T_g, the latter being evidenced from the drift in tan δ maxima. All the DMA spectra manifested two tan δ maxima. This implies a heterogeneous morphology for the network. The transition at low temperature that principally determines the high temperature serviceability of the system can be ascribed to the epoxy-dominated reaction products, possibly the oxazolidinone part. The temperature corresponding to this increases only marginally even on enhancing the cyanate concentration in the blend significantly, implying that the composition or structural features responsible for this transition is not significantly altered by the composition. The second transition, occurring at around 250°C, corresponds in all probability to the polycyanurate as the glass transition of pure polycyanurate occurs at this temperature. The DMA spectra of various blend systems are shown in Figure 4. The composition dependency of the temperature of first transition (taken as the tan δ maximum) is shown in Figure 5. The presence of EPN reduces the T_g of polycyanurate by 90–100°C. This can adversely affect the dimensional stability and high-temperature performance of CEPOX systems.

Physical Properties

Coefficient of Thermal Expansion (CTE)

Materials meant for structures, particularly in aerospace applications, are expected to possess a high degree of dimensional stability. To achieve this, they require minimum CTE, preferably near-zero values. Cyanates generally fall into this class. High CTE and large differences in CTE between the resin and reinforcement of composite structures led to matrix microcracking and dimensional instability during thermal cycling. The effect of incorporation of EPN into CE matrix on the CTE of the resultant matrix was of interest.

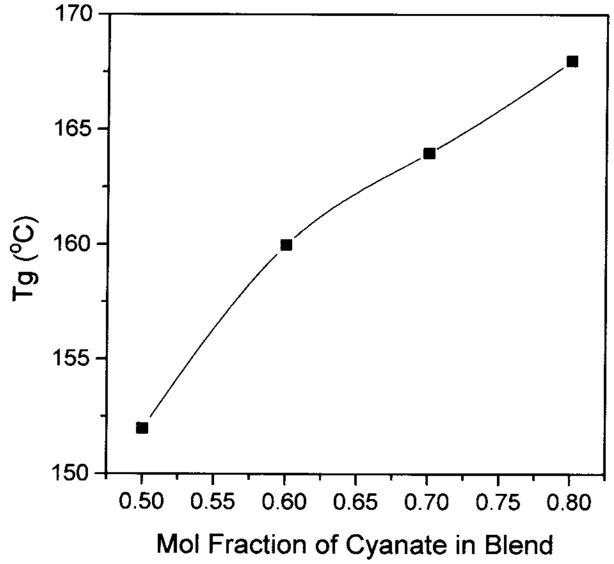


Figure 5 Dependency of the T_g of poly(oxazolidinone) phase on blend composition.

Table III Physical and Dielectric Properties of BACY and CEPOX Blends (neat)

Resin	Moisture Absorption (%)	Dielectric Constant (1 MHz, 60% RH)	Dissipation Factor (tan δ)	CTE (10^{-5}/°C)	
				25–70°C	70–100°C
CEPOX-1	1.53	3.67	0.021	5.25	7.10
CEPOX-2	1.46	3.72	0.017	4.85	6.50
CEPOX-3	1.47	3.70	0.016	4.90	7.00
CEPOX-4	1.54	3.67	0.016	4.85	6.70
BACY	1.49	3.61	0.022	4.80	6.00

The CTE of the coreacted resin was examined as a function of its composition by TMA at a heating rate of 5°C/min. The values were found to increase marginally with an increase in the epoxy content in the system. BACY possesses a CTE of 4.80×10^{-5}/°C up to 70°C, which is practically unaffected by blending with small quantities of EPN. At a higher temperature, the effect is more pronounced. Table III compiles the CTE values at two different temperature zones for the cured, neat CEPOX resins. The CTE is found to be higher at a higher temperature for a given stoichiometry. However, the change in CTE with composition is within acceptable limits.

Moisture Absorption

Materials meant for space vehicle components must pass the stringent requirement of minimum moisture absorption. Materials absorb water from the earth's atmosphere that will be degassed in outer space. This let-out moisture may condense on the surfaces of sensitive optical devices, affecting their performance adversely. Moreover, excessive water absorption can lead to dimensional instability of structures also.[31] Therefore, matrix resins meant for composites for critical satellite structural applications require minimum moisture absorption characteristics. Conventionally cured epoxy resins absorb moisture to around 4–5% because of the presence of —OH groups, which bind water through H bonding. Previous studies have already shown that the moisture absorption of cyanate or cyanate/epoxy blend was considerably less than that of the epoxy resin.[32,33] Cyanate esters are preferred to epoxies in critical applications in satellite structures for this reason.[31] It was of interest to see how this property is affected when BACY is blended with different proportions of EPN. The observation in the present case is also in line with the reported one. The weight gain of the specimens after exposure to boiling water for 24 h gave values comparable to that of pure BACY as given in Table III. Even though enhanced polarity can be expected for the oxazolidinone-containing networks, their moisture absorptivity is of the same order as that of the polycyanurates. The increase caused by the generation of oxazolidinone rings in the network is practically negligible.

Dielectric Properties

One of the salient features of cyanate ester (CE) is its symmetric structure, rendering its dielectric constant (Dk) very low among the common thermosets. The dissipation factor is also known to be very low.[34] These characteristics render it the preferred material in printed circuit boards (PCBs) meant for high-speed circuitry.[35,36] The circuit speed is inversely proportional to the square root of the dielectric constant and the electrical energy dissipated as heat is proportional to the product of dielectric constant and dissipation factor (tan δ). The latter is a measure of the loss of current or heat dissipated from electrical energy. Because of their low Dk and tan δ, CE and their composites are preferred in microwave-transparent structures such as radomes in the place of conventional glass/epoxy systems.[36] A material ideally suited for such applications should have the lowest dielectric constant and tan δ values. It should also possess low moisture absorption and high T_g, because moisture absorption increases the dielectric constant and lowers T_g and dimensional stability.

The data given in Table III show that the increase in dielectric constant is negligible on blending polycyanurate with oxazolidinone. The value is close to the reported value of 3.0 for CE under dry conditions.[34] Interestingly, the dissipation factor showed a tendency to decrease on reacting the CE with epoxy system.

Table IV Thermal Stability of Cured BACY and CEPOX Systems

Resin (cured)	T_i (°C)	T_p (°C)	T_e (°C)	Char Yield at 600°C (%)
CEPOX-1	270	402	485	29.2
CEPOX-2	280	401	490	29.6
CEPOX-3	290	390	490	30.0
CEPOX-4	310	413	480	29.4
BACY	425	459	480	46.0

Thermal Characteristics

The thermal stability of the cocured systems was investigated by thermogravimetric analysis. It was found that the incorporation of oxazolidinone led to a substantial decrease in thermal stability of the network. In fact, the initial decomposition temperature (T_i) decreased and the rate of thermal degradation increased proportional to the epoxy content in the blend. Formation of oxazolidinone decreases thermal stability for two reasons. It is aliphatic in nature and its formation decreases the effective crosslink density. Similar observations were reported.[11] Table IV gives the thermal decomposition characteristics as well as anaerobic char yields (at 600°C) for the cured CEPOX and BACY systems. The presence of oxazolidinone rings reduced the initial decomposition temperature T_i and the temperature of maximum decomposition T_p. The char yields were more or less the same among the CEPOX resins (30%) and much lower than that of BACY (by about 16%). A slight increase in T_i value can be seen with increasing triazine content. Since decompositions are initiated at the oxazolidinone sites, there is a rapid fall in T_i on changing from pure triazine to oxazolidinone triazine.

Studies on Glass Laminate Composites

There have been a number of studies on cyanate–epoxy systems as applied to composites. The majority of the published work does not give detailed information on processing and the resin chemistry probably owing to their technological importance. In fact, most of the work is patented.[4] A large number of patent applications refer to the application of the cyanate–epoxy formulations in printed circuit boards, but practically none of them deals with the matrix on the basis of pure cyanate–epoxy blend. Usually, other components capable of coreacting with both systems (particularly with epoxy) such as anhydrides, amines, acids, etc. are blended.[4] CEPOX systems using advanced epoxies and cyanates along with graphite reinforcement were studied for aerospace applications, but the information divulged is minimal.[37] Systematic studies on neat resin or composite properties and their compositional dependency were not covered in the literature. In this work, glass-laminate composites of the blends of varying compositions were molded under pressure by employing the same high-temperature cure schedule as for the neat resin molding, and their mechanical properties were monitored as a function of the composition of the matrix.

Cure Optimization of Prepreg by DMA

The optimization of the cure schedule for the composite was arrived at by DMA studies by using the prepreg. Although DSC technique can indicate the cure initiation and completion temperatures, it cannot be fully relied on to monitor cure reactions associated with very little enthalpy change. Generally, thermosetting reactions become diffusion controlled toward the end of the reaction, as is the case with cyanate ester and its blends. The result is that the reaction becomes very slow toward the end. Because the heat generated, or rather, the DSC signal at this stage becomes insignificantly low, DSC cannot detect reactions taking place during this time. In such a situation, the DSC analysis has to be complimented by DMA. The latter senses change in mechanical strength (i.e., modulus), which is highly sensitive to minor chemical changes, especially toward the end of the reaction. Hence, for cure optimization of the CEPOX blend, DMA analysis was carried out with a single-ply laminate. The results were useful for the cure optimization of both neat resin and its composite.

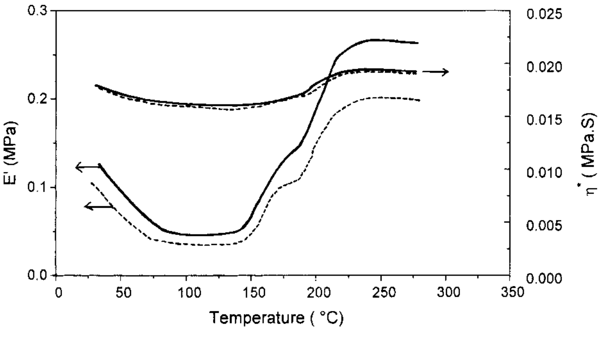


Figure 6 DMA of prepregs (dynamic mode). (- - -) CEPOX-1, (——) CEPOX-3. Heating rate: 5°C/min.

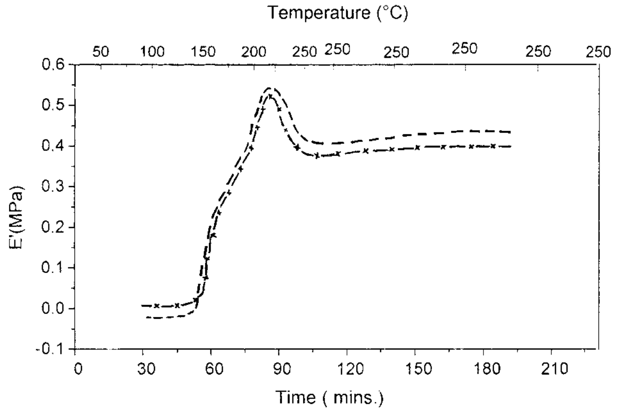


Figure 7 DMA of prepregs (dynamic and isothermal mode). (——) CEPOX-1, (- - -) CEPOX-3. Heating rate for dynamic part: 5°C/min.

The DMAs performed under dynamic heating condition, typically shown in Figure 6 for CEPOX-1 and -3, show a bimodal nature of the cure reaction. Cure is initiated at 150°C when E' starts increasing and the cure is completed at 225°C when it stagnates. At around 170°C, the cure reaction follows a different path. Although the exact nature and cause of this change of reaction path was not investigated here, it is in line with published information on cure mechanism, which predicts a sequential, multiple-step reaction as described above. It can be concluded that the first step is associated with trimerization of cyanate groups that takes place at a lower temperature regime, and the second step, with the formation of oxazolidinone either through direct reaction of epoxy with cyanate or through reaction of the initially formed triazine with epoxy, in line with established mechanisms.[8,9,29,30] Formation of oxazolidinone can be associated with relatively less increase in modulus because it is a flexible moiety and does not contribute to crosslinking significantly. The two-stage cure was manifested in all cases of CEPOX. Dynamic heating shows that the cure reaction is apparently complete at 225°C. However, to derive a clearer picture, isothermal DMA of the prepreg was done at 250°C and is shown in Figure 7. In this case, dynamic heating was applied until 250°C was reached, followed by isothermal heating at this temperature. It is found that after an initial drop, E' stagnates in about 50–60 min at this temperature. The drop is due to the glass transition of the partly cured matrix at this temperature. On the basis of this information, samples of CEPOX were subjected to a final cure at 250°C for 1 h. Composites required shorter cure times than the corresponding neat resins because the presence of functional groups on the surface of the reinforcements provided additional reaction sites and catalysts, enhancing the cure rate. For molding convenience, the systems were heated in a stagewise manner.

Mechanical Properties of Composites

In the present work, the mechanical properties of the glass-laminated composites, cured under identical conditions, were investigated as a function of the resin composition. The results are given in Table V. It is found that there is an improvement in ILSS as the resin accommodates more epoxies. The fiber wetting is promoted by the more polar and less viscous EPN and its cured product, [i.e., poly(oxazolidinone)]. However, formation of oxazolidinone adversely affects the high-temperature performance of the composites as evident from a sharp decrease in ILSS at 150°C. Moreover, the extent of retention of ILSS at this temperature decreases proportional to the oxazolidinone content in the network. The flexible, low T_g oxazolidinone moieties ease the composite interface, which accounts for the observed reduction in property. The good bonding pro-

Table V Mechanical Properties of E Glass-Reinforced Laminates of CEPOX and BACY

Matrix	(0°) Compressive Strength (MPa)	Flexural Strength (MPa)	ILSS (MPa) Ambient Temperature	ILSS (MPa) 150°C	ILSS (MPa) % Retention at 150°C
CEPOX-1	270	410	61	29	47.5
CEPOX-2	222	490	67	37	55.2
CEPOX-3	156	400	60	34	56.7
CEPOX-4	208	485	44	—	—
BACY	293	501	58	38	65.5

moted by EPN was, however, not translated to the flexural or compressive strengths of the composites. The flexural strength was found to generally decrease as the oxazolidinone content increased. This is contrary to the result for the neat resin wherein the flexible oxazolidinone rings contributed to enhance the strength. Because blending results in stronger interphase, the failure can be expected only in the matrix. If this is the case, the flexural strength of the composite should have shown an increasing trend with an increase in epoxy content. The inverse trend observed implies that the network structure, formed in the presence of the glass reinforcement, could be different from that in the neat resin. The reverse trend in flexural strength of the neat resin and that of the composite observed here substantiates the general observation that neat resin properties cannot be extrapolated to the composite on a one-to-one basis. Similar observation was made in another study on the nonreactive blend of cyanate ester and bismaleimide.[6]

The compressive strength, however, shows an initial decrease and then an increase with increasing oxazolidinone content. It appears that the strength diminishes as the matrix attains a more heterogeneous composition. Pure BACY has a uniform network and CEPOX-1 tends toward homogeneity (formation of more of oxazolidinone). Intermediate compositions (i.e., between BACY and CEPOX-1) have more heterogeneous network structures, which appear to be less resistant to compressive loads.

CONCLUSION

The blends of a novolac epoxy resin and BACY coreact to form crosslinked networks of which mechanical, physical, thermal, and laminate-composite properties depend on their composition. The binary system apparently showed a single-step curing in DSC, whereas multiple step curing was manifested in DMA analysis. The cure reaction conditions were optimized by DMA. The FTIR spectrum of the cured polymer indicated the presence of both cyanurate and oxazolidinone, in league with published literature in this respect. The mechanical properties of the neat resin moldings of the blend were, by and large, inferior to those of the pure polycyanurate, although the presence of flexible, aliphatic oxazolidinone rings in the blends is conducive for increasing the flexural strength. Tensile strength was decreased by the formation of oxazolidinone. A trend in compositional dependency of mechanical properties of the laminated composite did not bear any correlation to that of the neat resin. Although the polar heterocyclic oxazolidinone favored a stronger interphase, the effect was not reflected in the flexural strength of the composite, which showed a decreasing trend with the increase in oxazolidinone content. The fact that the increased flexural strength of the neat resins was not translated to the composite implied complex failure mechanism of the composite under flexural stress and the possibility for a different matrix composition in the composite in comparison to the neat resin molding. The CTE values of CEPOX resins at higher temperature increased with increasing epoxy content in the blend. The dielectric properties and moisture absorption of the cured blend did not show major deviation from those of the pure polycyanurate. The thermal stability of the oxazolidinone-modified cyanurate decreased in proportion to the concentration of the relatively less thermally stable oxazolidinone rings in the matrix. A similar trend was observed in the T_g of the network also, wherein the flexible aliphatic rings eased the rotation of the chains more than the rigid triazine.

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