Cure Behavior of Epoxy-Cyanate Ester Blend in Composite Systems: Evaluation Studies in Neat Resin Cast by Thermal and FTIR Techniques

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ABSTRACT: The post-cure behavior of a commercially available DGEBA-based epoxy modified cyanate ester resin (1,1-bis (4-cyanato phenyl) ethane) was investigated by thermo analytical techniques and Fourier Transform Infrared (FTIR) spectroscopy. Thermally initiated resin cure was carried out at 170°C/1 h followed by 180°C/2 h. Two different post-cure procedures, (PCPs), PCP-I (210°C/2 h + 250°C/1 h) and PCP-II (280°C/3 h), were independently followed for the cured resin material. Dynamic mechanical analysis (DMA) characterization of the resin casts indicated significant lowering of glass transition temperature (T_g), by about 35°C in PCP-II casts in comparison with PCP-I, though the former was post cured at higher temperature. However, the PCP-II specimens recorded considerable enhancement in storage modulus values at room temperature and above till about the T_g region. FTIR spectroscopic studies of the resin cast support the formation of both cyanurate triazine ring (1563 cm^{-1}, 1368 cm^{-1}) and oxazolidinone ring (1736 cm^{-1}) for the PCP-I resin cast while in the PCP-II specimens the former, namely the cyanurate formation was found to be absent. The absence of rigid cyanurate triazine rings in PCP-II was further strengthened by the tanδ $_{max}$ values observed in these resin casts by DMA. The DMA and differential scanning calorimetry gave comparable T_g values for both the PCP-I and PCP-II resin casts. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2023–2028, 2008

Key words: cyanate ester; dynamic mechanical analysis; differential scanning calorimetry; fourier transform infrared spectroscopy; triazine; oxazolidinone; glass transition temperature

INTRODUCTION

Thermosetting polymer composites have established their worth as structural materials in aerospace applications by virtue of their high specific strength properties. They have also proved their significance as the choice materials for avionic radomes and electronic packaging applications, wherein their dielectric loss properties drive the functional design. Sustained supersonic flights, miniaturization of electronic systems etc. have proved to be major driving factors towards development of newer class of polymer resin systems with enhanced glass transition temperatures (T_g) to meet stringent operating temperature requirements. In this context, the Cyanate esters (CE), which are a new class of high performance thermosetting resins having T_g as high as 300°C or more, are proving their worth as attractive candidates, since the conventional epoxies are limited in their applications upto a temperature of nearly 175°C. In addition to their superior thermal withstandability, CE materials also possess low dielectric loss properties in comparison with epoxies, which render them more suitable for high density PCB (Printed Circuit Board) applications. Cyanate esters are essentially esters of bisphenols and cyanic acid. Curing of cyanate esters occurs via polycyclotrimerisation.[1] Hamerton and Hay,[2,3] Reghunadhan Nair et al.[4] have presented a detailed account of the recent developments in cyanate esters viz. chemistry, technology and applications. However, owing to their inherent brittleness as cured materials and processing problems related to their flow characteristics, they are generally blended with different thermoplastics or epoxies for optimal characteristics in terms of processing ease and temperature withstandability. The T_g values of these blends are lower compared with their parent cyanate esters. However, better processability and lower costs are the derived benefits.

Among the blends Epoxy/CE have been explored as polymer matrix in high performance composites for aerospace and electronic applications. Improvement of tack and drape characteristics were reported as a function of type and concentration of epoxy used in these blends.[5] Bauer et al.[6–8] examined
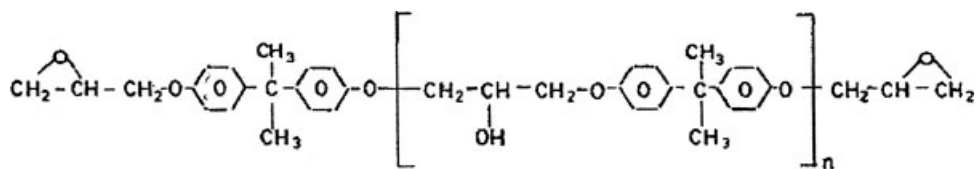
Figure 1   Structural formula of DGEBA.

model compounds and proposed a complex reaction mechanism in such epoxy/CE blends. Fyfe et al.[9] reported the possible cross-reactions between cyanate ester and epoxy resins. Lin postulated a new sequence of the mechanism by studying cure reaction of aromatic cyanate ester with different types of epoxies.[10] Effect of epoxy group concentration on the final structure of the epoxy/CE blends and reactivity of the two monomers in these blends in the presence of different catalysts are also reported.[11] Fourier transform infrared (FTIR) spectrum of the cured matrix of novolac-based epoxy and bisphenol A based cyanate ester indicated the presence of both cyanurate and oxazolidinone.[12] DMA studies revealed reduction in glass transition temperature with increasing epoxy in the PEI toughened cyanate-epoxy blend resins.[13]

In the present investigation, effect of different post cure procedures (PCPs), of a typical epoxy modified cyanate ester resin on the formation of chemical functionalities of the cured matrix and their glass transition temperature values are reported. Thermoanalytical techniques viz. DMA, DSC, and FTIR were used in the study.

MATERIALS AND METHODS

FINESET NCO-2001, a cyanate ester resin based on Bisphenol E (1,1-bis (4-cyanato phenyl) ethane) modified with DGEBA-based epoxy, supplied by M/s Fine Finish Organics Pvt. Ltd., Mumbai, India, was used in the studies. The stoichiometric ratio of cyanate ester to epoxy, as reported by the manufacturer, was 1.4 : 1 by weight. Figures 1 and 2 show the monomers of DGEBA and Bisphenol E Dicyanate, respectively.

The resin was cast in a mold of 150 mm × 150 mm × 5 mm. It was cured at 170°C/1 h + 180°C/2 h in an air circulated oven. The cured resin cast sample cut into three equal pieces of approximate dimensions 150 mm × 50 mm × 5 mm. Of these three, one piece was not subjected to any post cure procedures. This piece is, hence, called Pre-PCP in this work. The second part was given a schedule of 210°C/2 h followed by 250°C/1 h. This program was symbolized as PCP-I in this work. The third and the last piece was given a single step post cure schedule of 280°C/3 h and this is abbreviated as PCP-II in this work. All the three, viz. Pre-PCP's, PCP-I and PCP-II's were used for characterization work as detailed below.

MATERIALS CHARACTERIZATION

1. Dynamic mechanical analysis (DMA) of cast resin specimens (of size 35 mm × 12.5 mm × 2.5 mm) was carried out using DMA 2980 supplied by M/s TA Instruments, USA, in single cantilever mode at 1 Hz frequency, 30 μm amplitude at a heating rate of 3°C/min from ambient temperature to 300°C. Three specimens from each category of resin casts were subjected to the study and the values reported are the average value of these measurements. The T_g values were read from the peak of temperature versus loss modulus curves.

2. Modulated Differential Scanning Calorimetry (MDSC) was carried out using DSC, Q100 make equipment from M/s TA Instruments, USA. MDSC is a high performance version of DSC in which a sinusoidal temperature wave is superimposed over traditional linear temperature program. The resulting oscillatory temperature and heat flow signals are deconvoluted into total, reversing and nonreversing heat flow. The heat flow from thermal events associated with temperature rate changes such as glass transition and melting are separated out in to the reversing heat flow while kinetic thermal events such as crystallization and chemical reactions are separated out in to the nonreversing heat flow. In the present study, the experiments were carried out in modulated mode with modulation amplitude of 3°C and modulation frequency of 30 s. The experiments were done in presence of nitrogen purge gas with a flow rate of 50 mL/min and maintaining a ramp of 3°C/min from ambient temperature to 300°C. Three specimens from each category of resin casts were subjected to the study and the T_g values
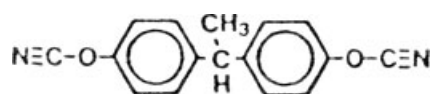

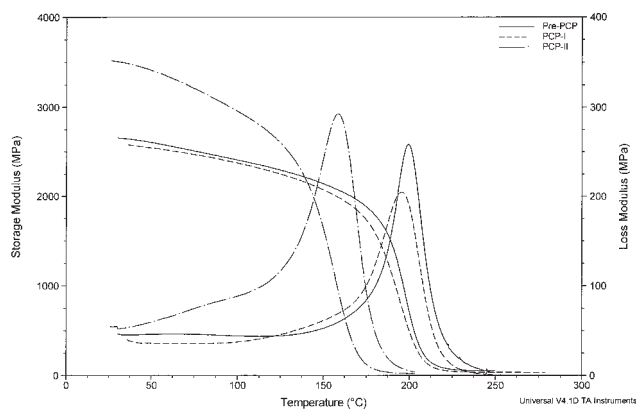Figure 2   Structural formula of bisphenol-E dicyanate.

Figure 3 DMA thermograms of epoxy/CE resin casts (Pre-PCP, PCP-I and PCP-II).

reported are the average value of these measurements. The temperature at which middle of the reversible heat flow change occurs was read as the T_g. The MDSC mode results confirmed the absence of nonreversible thermal events in the cured/post cured samples.

3. Thermo gravimetric analysis (TGA) of resin samples was carried out using TGA Q500 of M/s TA Instruments, USA at a heating rate of 3°C/min from ambient temperature to 280°C.

4. FTIR Spectra were recorded using Perkin–Elmer make spectrum-1 instrument. The samples were taken in potassium bromide (KBr) Pellet form, with spectral width 4000–450 cm^{-1}, average number of scans 10 and resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Figure 3 shows, DMA thermograms of the Pre-PCP, PCP-I and PCP-II resin samples. The resin cast which was, subjected to curing (170°C/1 h + 180°C/2 h)
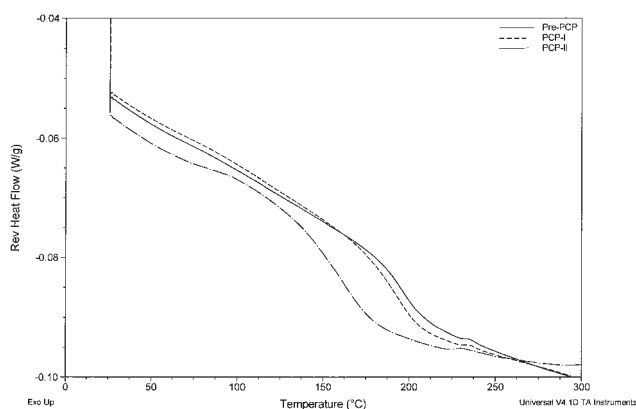
TABLE I
Glass Transition Temperature of Epoxy/CE Resin Casts

Property	Glass transition temperature, T_g (°C)		
	Pre-PCP	PCP-I	PCP-II
DMA	201 (5.7)	197 (5.0)	159 (6.1)
DSC	196 (2.5)	194 (2.5)	162 (4.9)

Values in parentheses are standard deviation of measured values.

recorded a T_g of 201°C. The resin which was, subjected to PCP-I schedule yielded a T_g of 197°C. PCP-II schedule, on the other hand, showed the lowest T_g (159°C). The above values were read from the peak of loss modulus curve. The results obtained by DSC (Fig. 4) were comparable with the DMA values of the glass transition temperature. From the DSC thermograms the T_g values of the Pre-PCP, PCP-I and PCP-II resin are 196, 194, and 162°C, respectively. The T_g values obtained by DMA and DSC were tabulated in Table I. Further, TGA study was carried out to identify thermal degradation, if any, between 250 and 280°C for Pre-PCP sample as PCP-II sample recorded substantial reduction in T_g compared with PCP-I. The study has shown a weight loss of 0.9% from ambient temperature to 250°C while a weight loss of 0.5% was recorded from 250 to 280°C (Fig. 5). Specifically there was no steep reduction in % weight between the maximum cure temperatures of PCP-I (i.e., 250°C) and PCP-II (i.e., 280°C) indicating the absence of thermal degradation in the cured resin binder. The reduction in T_g values in PCP-II may be a result of chemical reaction during post cure leading to different groups or molecular chains. IR spectrum of neat resin (Fig. 6), as per supplier, shows (i) absorption peaks at 2266 and 2237 cm^{-1}, which correspond to the O—C≡N stretching group, which normally appears as a doublet, (ii) a peak at 916 cm^{-1} that corresponds to the absorption of epoxy and (iii) presence of peak at 830 cm^{-1}
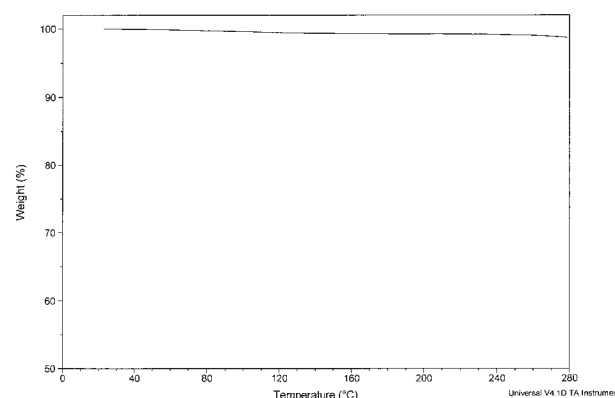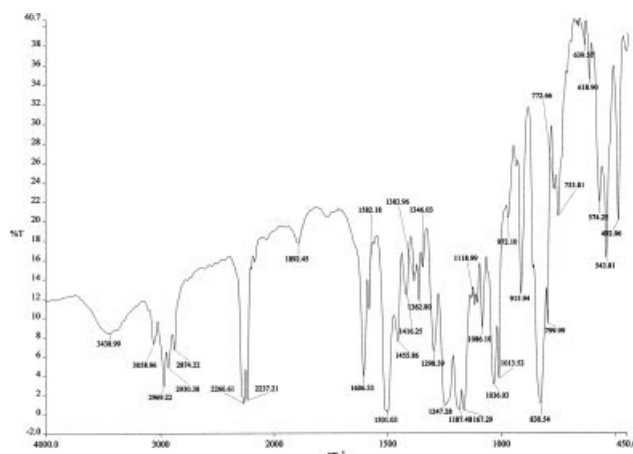

Figure 4 DSC thermograms of epoxy/CE resin casts (Pre-PCP, PCP-I and PCP-II).

Figure 5 TGA thermogram of Pre-PCP sample.

Figure 6 FTIR spectrum of epoxy/CE resin (Neat).

Figure 8 Copolymerization reaction of epoxy/CE blend.

corresponding to para substitution of aromatic ring. The peak at 830 cm^{-1} is seen in every stage, i.e., whether belonging to Pre-PCP or PCPs. The broad absorption at 3439 cm^{-1} is attributed to the secondary hydroxyl of the epoxy molecule. IR spectrum of Pre-PCP resin cast recorded (Fig. 7) absorptions of triazine ring at 1564 cm^{-1} (C=N—C) and 1367 cm^{-1} (N=C—O) and oxazolidinone carbonyl at 1756 cm^{-1}. The appearance of peaks at 1459 and 1691 cm^{-1} is suggestive of the partial formation of the isocyanurate from the triazine structure. This clearly indicates conversion of all the cyanate groups and epoxy groups to either triazine or oxazolidinone rings. The reaction path, as shown in Figure 8, suggested by Bauer et al.,[6–8] gets support from these observations. As per this scheme, the main reactions occurring during cyanate ester - epoxy curing are (1) trimerization of **cyanate (2)** insertion of glycidyl ether into **cyanurate (3)** isomerization of alkyl substituted cyanurates to **isocyanurates**
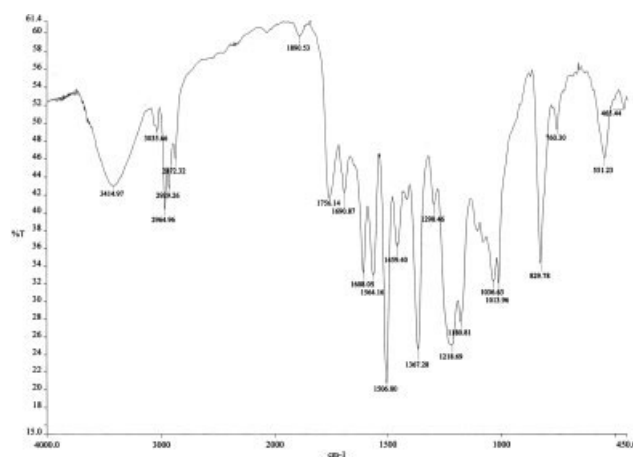
(4) build-up of oxazolidinone. IR spectrum of resin cast at PCP-I stage (Fig. 9) shows the presence of rigid triazine absorption peaks of cyanurate (1563 cm^{-1}, 1368 cm^{-1}), isocyanurate (1456 cm^{-1} and 1700 cm^{-1}) and oxazolidinone (1736 cm^{-1}) groups. This is suggestive of additional conversion of cyanurate to isocyanurate through isomerization in the PCP-I stage. A significant reduction (20 cm^{-1}) in the oxazolidinone carbonyl frequency combined with a reduction in the hydroxyl stretching band frequency (from 3415 to 3404 cm^{-1}) is suggestive of possible hydrogen bonding between the hydroxyl and the oxazolidinone carbonyl. The chemical groups and associated peak positions in each stage of cure/post cure of the resin specimens are tabulated in Table II.

The IR spectrum of resin cast at PCP-II stage (Fig. 10) gives support to the complete conversion of cyanurate to isocyanurate as evidenced by (i) the absence of triazine absorptions at 1564 cm^{-1} and 1367 cm^{-1} and (ii) the presence of isocyanurate frequencies at 1453 cm^{-1} and 1697 cm^{-1}. The observation of hydroxyl stretching frequency in the PCP-II coupled
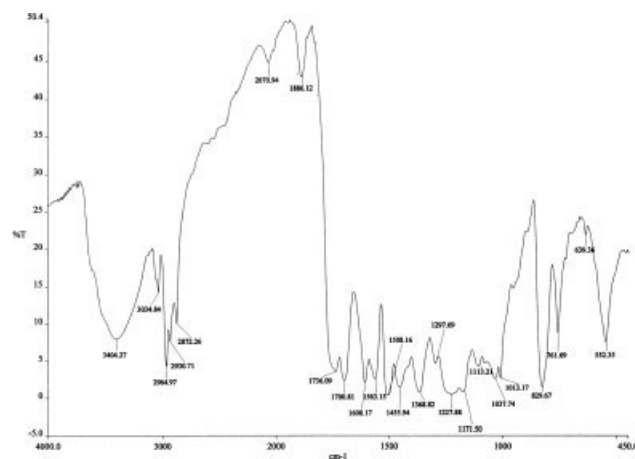

Figure 7 FTIR spectrum of Pre-PCP epoxy/CE resin.

Figure 9 FTIR spectrum of PCP-I epoxy/CE resin.

TABLE II
IR Spectral Changes of Epoxy/CE Resin Casts

Chemical group	Peak positions (cm^{-1})			
	Neat resin	Pre-PCP	PCP-I	PCP-II
Epoxy	916	–	–	–
Cyanate	2266, 2237	–	–	–
Cyanurate	–	1564, 1367	1563, 1368	-
Isocyanurate	–	1459, 1691	1456, 1700	1453, 1697
Oxazolidinone	–	1756	1736	1735

TABLE III
Viscoelastic Properties of Epoxy/CE Resin Casts

Property		Cure History		
		Pre-PCP	PCP-I	PCP-II
Storage	$\cong$Ambient	2513 (90)	2562 (80)	3408 (67)
modulus	120°C	2358 (84)	2353 (76)	2685 (70)
(MPa)				
Tan δ_{max}		0.6219 (0.01)	0.5424 (0.05)	0.7291 (0.02)

Values in parentheses are standard deviation of measured values.

with the reduction in the frequency of oxazolidinone carbonyl again emphasize the possible formation of hydrogen bonding. The isocyanurate formed in PCP-I and PCP-II stages could not further react with epoxy since stoichiometric quantities of epoxy groups are not available for conversion. The near total conversion of cyanurate to isocyanurate and the subsequent absence of the rigid triazine groups are responsible for substantial reduction in T_g in PCP-II sample (159°C) compared with the Pre-PCP stage resin, which as discussed earlier, recorded a T_g of 201°C. However, the storage modulus (SM) value of the PCP-II cured resin has increased significantly compared with PCP-I resin, in the region of room temperature up to 120°C, where the glass transition behavior begins. The viscoelastic properties like SM and tan δ_{max} were tabulated in Table III. The SM value at about ambient temperature of PCP-II resin is 3408 MPa and PCP-I resin is 2562 MPa. The corresponding SM values at a higher temperature, namely, 120°C are 2685 and 2353 MPa, respectively. It can be inferred that the PCP-II specimen has recorded highest value of SM at temperature upto 120°C, thereby, proving PCP-II procedure yields higher stiffness in the material. This will be a useful input for engineering applications, where the composite material system is required to withstand maximum use temperature in the range of 120°C. On the
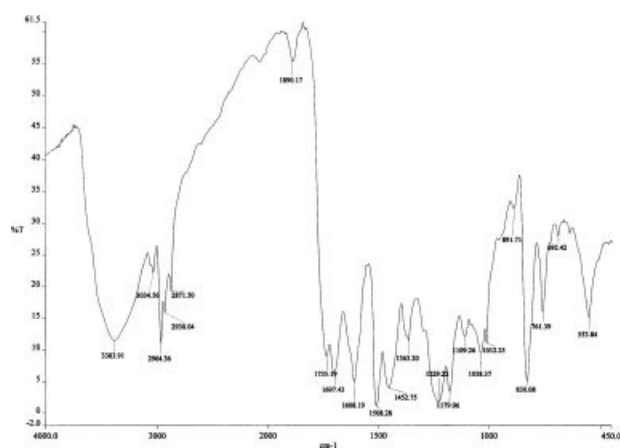
other hand, the behavior of having higher modulii though having aliphatic backbone in PCP-II samples, however, remains to be explained. Similar unexplainable observations were reported by Hwang et al.[14] in which DCPDCY (2,6-Dimethyl phenol dicyclopentadiene dicyanate ester) having the cycloaliphatic structure of DCPD (Dicyclopentadiene) ring had significantly higher modulus than cured BADCY (Bisphenol A dicyanate) having aromatic character. Further research efforts are needed in this direction. Tanδ_{max} of the resin at Pre-PCP, PCP-I and PCP-II stages are 0.6219, 0.5424, and 0.7291, respectively. The decrease in tan δ_{max} value of PCP-I compared with Pre-PCP is suggestive of formation of rigid molecular chains in the sample. The increased flexibility in the molecular chain of PCP-II resin cast is indicated by corresponding increase in the tan δ_{max} compared with the Pre-PCP stage values. In other words, absence of rigid aromatic cyanurate groups in PCP-II sample has yielded an increase in tan δ_{max} value.

CONCLUSIONS

Two different postcure procedures PCP-I and PCP-II were independently followed for a commercially available epoxy/CE resin blend. The PCP-II samples showed decrease in the glass transition temperature significantly though post curing was done at higher temperature compared with PCP-I. Nevertheless, it increased the storage modulus substantially when compared with PCP-I samples. This decrease in glass transition temperature was attributed due to the absence of rigid cyanurate triazine group as revealed through IR spectroscopy. Hence, the epoxy/CE resin blend can be used at different postcure stages (PCP-I and PCP-II) as a polymer matrix in composites by way of optimizing mechanical properties and maximum use temperatures.

Figure 10 FTIR spectrum of PCP-II epoxy/CE resin.

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