Viscoelastic properties and morphology of dicyanate ester/epoxy co-polymers modified with polysiloxane and butadiene–acrylonitrile rubbers

Urszula Szeluga · Paweł Moryc

Received: 13 July 2012 / Accepted: 13 December 2012 / Published online: 16 January 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract Dynamic mechanical analysis was conducted on specimens prepared from cyanate ester (CE) and epoxy (EP) resins cured together at various mass compositions. Increase of amount of epoxy resin in composition was shown to have a disadvantageous effect on glass transition temperature (T_g). It was shown that post-curing procedure was needed to produce a polymer matrix with a single glass transition relaxation, but increase in post-cure temperature up to 250 °C resulted in slight reduction in T_g for epoxy/cyanate copolymers. TG results proved that the presence of epoxy resin reduces thermal stability of the cyanate/epoxy materials. The neat CE and EP/CE systems containing 30 wt% of epoxy resin were modified using epoxy-terminated butadiene–acrylonitrile rubber (ETBN) and polysiloxane core–shell elastomer (PS). The scanning electron microscopy (SEM) results showed the existence of second phase of ETBN and PS modifiers. Only in the case of EP/CE composition modified with ETBN, well-dispersed second phase domains were observed. Analysis of SEM images for other CE- and EP/CE-modified systems revealed the formation of spherical aggregates.

Keywords Cyanate/epoxy copolymers · DMA · Modification · Morphology · Thermal stability

Introduction

Polycyanurates are interesting polymers used in the area of aerospace structures, dielectrics, aircraft, and others requiring special materials. These applications result from their excellent properties such as high performance of mechanical properties, low dielectric loss properties, low out-gassing during curing, low toxicity, and moisture absorption [1]. In the curing reaction, three cyanate ester functional groups (–OCN groups) form a triazine ring. Due to the high degree of symmetry in the triazine ring, where dipoles associated with the carbon–nitrogen and carbon–oxygen bonds are counterbalanced, polycyanurates have low relative permittivity in general. It is a potential dielectric matrix for composites. But like other thermosets, cyanate esters have high cross linkage which makes it fragile and limits its usage in some cases requiring good mechanical properties [2–4]. Relatively high price and high brittleness are the drawbacks and the reasons why cyanate esters are modified [5]. The improvement of flexibility can be achieved by various types of modifications.

Three main methods as follows are known and used:

- Copolymerization with epoxy resin [1, 5–7]
- Blending cyanate ester resin with thermoplastic resins, for example polysulfone [8, 9], polyarylate [10], poly(ether imide), polycarbonate, polyamide [11]
- Application of reactive elastomers [12, 13].

When modifiers are used, the main task is to control the morphological structure which is necessary to achieve significant toughening. Copolymerization with epoxy resin is the most important method, and it allows for modification of properties such as glass transition temperature, mechanical properties, and adhesion while reducing the cost. The chemistry of cyanate ester-epoxy systems has

U. Szeluga (✉)
Center of Polymer and Carbon Materials, Polish Academy
of Sciences, Marii Curie-Skłodowskiej 34, Zabrze, Poland
e-mail: urszula.szeluga@cmpw-pan.edu.pl

P. Moryc
Faculty of Chemistry, Silesian University of Technology,
Marcina Strzody 9, Gliwice, Poland

been examined and documented [1, 2, 13–15]. The reaction pathway is complicated and implies several reaction steps as is shown in Scheme 1.

Upon heating, cyanate ester functional groups will undergo a cyclotrimerization reaction to form a triazine linkage. The epoxide functionality also reacts with other epoxide groups to form a polyether. Also, the epoxide reacts with the triazine to form a five-membered oxazoline ring. Each of these reactions occurs in varying amounts depending on the ratio of the blend.

One of the most successful modification methods for thermosets is the incorporation of second rubbery phase that separates from the matrix during curing, leading to different morphologies [16–19]. The advantage of rubber toughening in thermosets is that fracture toughness can be improved dramatically. However, this modification will lead to significant reduction in the modulus and thermal stability of the material.

In recent years, high-performance thermoplastics have been used to modify thermosetting resins such as PES, PEI, PEEK, ABS, etc., because of their high modulus and glass

transition temperatures [8, 9, 11, 20]. The incorporation of thermoplastics, initially miscible in epoxy resin and creating second phase during the epoxy-hardener curing reaction, leads to toughness improved polymer networks.

In this study, co-polymers based on bisphenol A dicyanate ester and diglycidyl ether of bisphenol A in different mass proportions were analyzed mainly by the use of dynamic mechanical analysis (DMA). DMA is a very useful method for studying cross-linked thermosets and allows to determine the viscoelastic properties as a function of temperature and frequency [2, 19, 21–24]. These co-polymers were modified using a core-shell polysiloxane elastomer and epoxy-functionalized butadiene-acrylonitrile copolymer. The dynamic mechanical properties (storage modulus and loss factor), microscopic characteristics (SEM), and impact behavior were determined. The influence of epoxy resin content and elastomeric modifiers was examined. These results constitute the supplement of the earlier study concerning the investigation of the curing reactions for the same systems by means of the DSC method [25].

Scheme 1 Schematic reaction pathway in the cyanate ester-epoxy systems

Experimental

Raw materials

The cyanate ester resin (CE), Primaset PT-15, a dicyanate ester of bisphenol A (DCEBA) with a cyanate equivalent of 139 g equiv^{-1} was kindly supplied by Lonza Ltd. The epoxy resin (EP) was a commercial grade prepolymer of the diglycidyl ether of bisphenol A (DGEBA) received from Brenntag Poland, as Epikote 828, with an epoxy group content of approximately $0.54 \text{ mol}/100 \text{ g}$. The catalyst system was made from 300 ppm of the complex metal copper(II) acetyl acetonate obtained from Merck and 4 phr of the co-catalyst nonylphenol from PCC Synteza S.A (Poland). Two types of impact modifiers were used to improve the mechanical properties. The first was the epoxy-terminated butadiene–acrylonitrile copolymer (ETBN) prepared from carboxyl-terminated copolymer Hycar 1300X8 CTBN (BF Goodrich Chem.) and epoxy resin. The second modifier was the composition of 4,4'-ethylidendiphenyldicyanate and core–shell polysiloxane rubber (PS), as Albidur XP1 received from Nanoresins AG. The mass fraction of ETBN rubber and polysiloxane was 10 wt%.

Sample preparation

Mixtures of cyanate ester and epoxy resins with different mass ratios (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 30/70) were prepared. The following mixing procedure was employed for all systems. The copper(II) acetyl acetonate was pre-dissolved in nonylphenol at 100°C , stirring continuously until a homogeneous mixture was obtained; then it was cooled to room temperature. The required amount of epoxy resin was mixed with the molten cyanate at $90\text{--}100^\circ\text{C}$ for approximately 5 min, and then the catalyst mixture was added and stirred to obtain a homogeneous mixture. To obtain samples modified with the epoxy-terminated butadiene–acrylonitrile and polysiloxane co-polymers, the required amount of modifier (10 wt%) was added to the mixture before catalyst system introduction. The completely cured materials were obtained by transferring the mixture after the preparation and degassing into the steel mold and placing it in the oven for 1 h at 180°C and 4 h at 220°C . All measurements were performed for samples cured exactly in this way. The neat cyanate and epoxy/cyanate co-polymer (30/70) were additionally post-cured 3 h at 250°C to check the influence of temperature conditions primarily on the glass transition temperature (T_g).

Measurements

Dynamic mechanical analysis (DMA)

The DMA was performed using DMA 2980 TA Instruments analyzer. The experimental values of the real part (storage modulus; E') and imaginary part (loss modulus; E'') of dynamic elastic modulus and loss tangent ($\tan \delta$) were obtained as functions of temperature. The testing mode was the bending dual cantilever clamp with samples having a cross-section $10 \times 4 \text{ mm}$ and length of 60 mm. The mechanical spectra at 1 Hz (with oscillation amplitude $10 \mu\text{m}$) were obtained using temperature scan rate of 3°C min^{-1} starting from 10°C and ending just above the glass transition temperature of cyanate and epoxy/cyanate specimens. The T_g of fully cured materials were taken to be the temperature at maximum of $\tan \delta$ peak at 1 Hz. The obtained data points were collected and analyzed using Universal Analysis NT Software.

Scanning electron microscopy (SEM)

The quality of dispersion of PS and ETBN in cyanate and cyanate/epoxy matrices was investigated by a scanning electron microscope model Quanta 250 (FEG, USA) with an accelerating potential of 10.0–15.0 kV. Microphotographs were taken on the fracture surface coated with gold.

Thermogravimetric analysis (TG)

Thermal stabilities of cyanate and cyanate/epoxy matrix were measured on a Q-1500 D thermogravimetric analyzer (Hungary) with the heating rate of 10 K min^{-1} under nitrogen atmosphere.

Results and discussion

Influence of the curing conditions on dynamic mechanical properties

The effect of epoxy resin content on viscoelastic properties of its mixtures with cyanate ester resin was examined for specimens in which the participation of epoxy resin was changed from 0 to 70 wt%. Figures 1 and 2 show the bending storage modulus and $\tan \delta$ curves for systems cured 1 h at 180°C , illustrating the changes in the thermal and mechanical properties of the polymer materials that occur when subjected to varying temperatures.

For the specimens without additional post-cure process, two $\tan \delta$ peaks were observed, which are denoted in

Fig. 1 Variation of the storage modulus with temperature for epoxy/cyanate mixtures cured at 180 °C: 1 neat CE, 2 EP/CE (10/90), 3 EP/CE (30/70), 4 EP/CE (50/50), 5 EP/CE (70/30)

Fig. 2 Variation of the loss factor with temperature for epoxy/cyanate mixtures cured at 180 °C: 1 neat CE, 2 EP/CE (10/90), 3 EP/CE (30/70), 4 EP/CE (50/50), 5 EP/CE (70/30)

Table 1 as T_{g1} and T_{g2} . This feature may be attributed to a low crosslink density and an incomplete formation of a fully integrated polymer network of these two polymer species. The increase in modulus after the first $\tan \delta$ peak in Figs. 1 and 2 is attributed to further crosslinking of the polymer due to exposure of the material to temperature in the post-cure range for significant amounts of time. The E' in the glassy region up to about 80 °C for all EP/CE networks cured only at 180 °C are higher than those of the neat CE resin.

The detailed data dependent on the composition are shown in Table 1. In the glassy and viscoelastic ranges, the largest influence of the temperature on the storage modulus is visible for the sample containing 70 % of EP and the smallest one for CE resin and the copolymer containing 10 % of EP. It can be concluded from Figs. 1 and 2 that together with the rise in the EP content, thermal stability becomes lower. It is caused by the greater mobility of the

Table 1 Viscoelastic properties obtained for different epoxy/cyanate mixtures cured at 180 °C

Sample	E'_{20} /MPa	T_{g1} / °C	T_{g2} / °C	$\tan \delta$
CE	1.963	205	311	0.78/0.34
EP/CE (10/90)	2.382	192	273	0.40/0.44
EP/CE (20/80)	2.493	206	271	0.31/0.45
EP/CE (30/70)	2.121	204	259	0.39/0.45
EP/CE (40/60)	1.945	205	249	0.48/0.40
EP/CE (50/50)	2.288	188	239	0.41/0.31
EP/CE (70/30)	2.592	105	—	0.47

E' storage modulus at room temperature, T_g temperature of loss factor peak, $\tan \delta$ loss factor maximum value

epoxy resin chains than those from cyanate. From the other side, co-polymers with the epoxy resin cured at 180 °C seem to be more toughened in the glassy state than CE resin.

The temperature range of a dramatic drop in modulus connected with the glass transition depends on the epoxy resin amount in the co-polymer, and it is moved in the direction of the low temperature more and more with increase in the epoxy resin content. These results are in agreement with preliminary expectations. EP resin is characterized by worse thermal properties than CE resin, that is, their addition should worsen the thermal stability of the copolymer to some degree.

The $\tan \delta$ curves including two peaks, T_{g1} and T_{g2} , were observed for all samples without post-cure of both neat cyanate and epoxy/cyanate mixtures. The analysis of $\tan \delta$ curves showed that the cyanate resin blending with a higher ratio of epoxy had worse thermal properties, showing a lower glass transition temperature, both T_{g1} and T_{g2} taken as maximum of $\tan \delta$ peak (Table 1). However, the difference between the T_{g1} and T_{g2} becomes smaller as the epoxy resin content increases. The decrease in T_g of EP/CE matrices, as a result of increase in epoxy content, was more evident for T_{g2} than T_{g1} .

The effect of post-curing conditions on viscoelastic properties was tested for samples of neat CE system and EP/CE co-polymers containing 30 wt% of EP initially cured at 180 °C and then conditioned 4 h at 220 °C. The second mode of post-cure was 4 h at 220 °C, and additionally, samples were placed for 3 h at 250 °C.

Dependence of the storage modulus and $\tan \delta$ courses on the post-cure conditions is shown in Figs. 3 and 4.

The conditions of post-cure procedure had a significant effect on the final thermal properties of compositions. The storage modulus increases together with post-curing process especially for neat CE matrix. When the temperature of post-curing increases, the drop in storage modulus is observed at higher temperature, which confirms the

Fig. 3 Influence of post-cure conditions on storage modulus and $\tan \delta$ for CE: 1 1 h at 180 °C, 2 post-cured 4 h at 220 °C, 3 post-cured 4 h at 220 °C and 3 h at 250 °C

Fig. 4 Influence of post-cure conditions on storage modulus and $\tan \delta$ for EP/CE (30/70): 1 1 h at 180 °C, 2 post-cured 4 h at 220 °C, 3 post-cured 4 h at 220 °C and 3 h at 250 °C

increase in the crosslink density in post-cured thermosets. In the case of the neat cyanate system, higher temperature of post-cure corresponded to higher T_g values. It has been shown, at the same time, that post-curing of EP/CE copolymer (30/70) at 250 °C had a negative effect on T_g and caused a decrease in the T_g .

Temperature of post-curing influences the width of $\tan \delta$ peak. The $\tan \delta$ peak width at half of peak height ($S_{1/2}$) for the cyanate post-cured at 220 °C is equal to about 48 °C. Post-curing at 250 °C results in the width being reduced to 33 °C. Post-cured samples are characterized by much lower $\tan \delta$ values, smaller area under $\tan \delta$ peak ($A_{\tan}$), and a greater homogeneity. It is visible from Figs. 3 and 4 that already after post-curing in 220 °C, two phases with different T_g disappeared, and a single peak with one T_g was formed.

The CE system in the case of sample post-cured and sample without post-curing exhibited a higher T_g than the EP/CE (30/70) system. Although post-curing at 250 °C resulted in a single and an intermediate T_g , in the case of EP/CE (30/70), it was found that increasing the post-cure

temperature lowered the T_g . This decrease in T_g at high post-cure temperatures was attributed to thermal degradation and reduction in crosslink density.

The detailed dynamic mechanical data dependent on the curing conditions are shown in Table 2.

The disadvantageous effect of the epoxy resin on the thermal stability of copolymers with the cyanate can result from the fact that oxazoline and oxazolidone ring coming into existence during the reaction of cyanate resin with the epoxy resin is characterized by a much lower thermal stability than the triazine ring created during curing of CE resin.

Dynamic mechanical analysis of completely cured epoxy/cyanate systems

DMA curves of original CE resin and the EP/CE copolymers completely cured (1 h at 180 °C and 4 h at 220 °C) are shown in Figs. 5 and 6. From data presented in both figures, it is evident that the addition of EP has negative effects on the thermal property of the co-polymers.

Table 2 Dependence of viscoelastic properties on curing conditions for CE and CE/EP (70/30) systems

Curing conditions	E'_{20}/MPa	$T_g/^\circ\text{C}$	$\tan \delta$
CE			
1 h at 180 °C	1.963	205	0.78
+4 h at 220 °C	2.368	285	0.44
+4 h at 220 °C + 3 h at 250 °C	2.394	289	0.39
CE/EP			
1 h at 180 °C	2.288	188	0.41
+4 h at 220 °C	2.355	241	0.40
+4 h at 220 °C + 3 h at 250 °C	2.269	221	0.31

Figure 5 clearly shows that the moduli of cured EP/CE co-polymers are lower than that of the neat CE resin when $T < T_g$. While at $T > T_g$, the storage moduli demonstrate the similar changeability. In rubbery-like region, the E' values at $T_g + 50^\circ\text{C}$ (E'_{rub}) of the co-polymers are significantly lower than that of the neat CE resin, and they decrease with an increase in epoxy content. The E'_{rub} of pure CE is equal to 97 MPa, while in the case of CE/EP copolymers containing 50 and 70 % of epoxy resin, the values are reduced to 57 and 47 MPa, respectively. Thus neat CE matrix has higher dimensional thermal stability than the co-polymers, and at the same time, the cured co-polymers are much tougher than the neat dicyanate ester resin. Reasons may lie in that the reaction between epoxy and cyanate groups would decrease the cross-linking density of the cured resin.

Figure 6 shows that the neat CE matrix has the highest intensity $\tan \delta$ peak, but EP/CE co-polymers have comparable $\tan \delta$ intensity. The smallest magnitude of loss factor is observed for 70/30 EP/CE co-polymer. T_g of neat CE and EP/CE co-polymers obtained as maximum of $\tan \delta$ indicate that the introduction of EP lowers the T_g values of

Fig. 5 Influence of the epoxy resin content on storage modulus. Samples cured 1 h at 180 °C and 4 h at 220 °C: 1 neat CE, 2 EP/CE (10/90), 3 EP/CE (30/70), 4 EP/CE (50/50), 5 EP/CE (70/30) **Fig. 6** Influence of the epoxy resin content on $\tan \delta$ curves. Samples cured 1 h at 180 °C and 4 h at 220 °C: 1 neat CE, EP/CE (10/90), EP/CE (30/70), EP/CE (50/50), EP/CE (70/30)

EP/CE co-polymers. The more the epoxy used, the lower the T_g value of the co-polymer is. Reasons for the above phenomena are the co-polymerization reaction between CE and epoxy, which is taking place in the system. The poorly thermal properties of epoxy lowered the thermal stability of the co-polymers based on cyanate and epoxy.

It is evident that post-curing at 220 or 250 °C results in a single glass transition relaxation, indicating that the crosslinked network is fully integrated at higher levels of curing. However, as the post-cure temperature is increased from 220 to 250 °C, the glass transition temperature decreases and the modulus decreases slightly for epoxy/cyanate systems. These two features indicate that thermal degradation of the matrix material is occurring to some degree, causing a reduction in crosslink density from the breaking of chain bonds.

Figure 6 shows the resulting T_g determined as $\tan \delta$ maximum temperature. The neat cyanate system exhibited the highest T_g . For epoxy/cyanate matrix, a considerable decrease in T_g with increasing epoxy resin content is visible. This is due to a higher content of lower thermally stable epoxy resin. Broad $\tan \delta$ transition suggests greater non-uniformity of cross-links in the CE system than in EP/CE co-polymers.

The main reason is the fact that the different backbone structures formed during the curing process have different physical properties. Neat CE has highly symmetric triazine ring crosslinking backbone and exhibits low toughness and high stiffness. For CE-rich blends, the highly symmetric triazine ring crosslinking backbone has been partially destroyed and replaced by some oxazoline and oxazolidinone structure. The oxazoline and oxazolidinone structures exhibit greater thermoplastic character and reduce the tensile strength [26]. Therefore, they have a higher toughness but lower stiffness than neat CE. For EP-rich blends, the main backbone of the crosslinking network is

polyether network, together with some oxazolidinone structure and rare triazine ring structure.

The detailed dynamic mechanical data dependent on the epoxy resin content in CE/EP are shown in Table 3.

The content of epoxy resin in co-polymer influences the width of $\tan \delta$ peak. The $\tan \delta$ peak width at half of peak height ($S_{1/2}$) for neat cyanate is equal to about 48 °C, and area under this peak is 7.1. The increase in epoxy resin content causes the width and area of $\tan \delta$ peak to be reduced. Epoxy/cyanate matrices are characterized by much lower $\tan \delta$ values, smaller area under $\tan \delta$ peak ($A_{\tan \delta}$), and so a greater homogeneity.

Thermal stability of completely cured epoxy/cyanate systems

The thermal stability of cyanate and cyanate/epoxy matrices was characterized by TG. Figure 7 shows changes in the mass of samples as a function of temperature. The data collected from the DTG curves are listed in Table 4.

As shown in Fig. 7 and Table 4, neat cyanate matrix is thermally stable before 430 °C and has an exothermic peak at 438 °C and is characterized by mass loss equal to 12 %. Compared with cyanate/epoxy co-polymers with various epoxy content, the thermal stability of neat cyanate system is the highest. The mass loss of neat epoxy matrix with an exothermic peak at 380 °C is about 33 %.

The results demonstrate that the addition of epoxy resin decreased the temperature at which the mass loss reached 5 wt%. The maximum degradation temperatures (T_m) of the epoxy/cyanate matrices with 30, 50, and 70 wt% epoxy resin are also lower than that of neat cyanate. These results prove that the presence of epoxy resin reduces thermal stability of the cyanate materials containing addition of epoxy. On the other hand, it can be seen that in the case of all cyanate/epoxy, also neat cyanate and epoxy matrices, up to about 400 °C, any significant thermal degradation effects are not observed. It should be remembered, on the

Fig. 7 TG curves of neat CE 1, EP/CE (30/70) 2, EP/CE (50/50) 3, EP/CE (70/30) 4, neat EP 5

Table 4 Thermal degradation temperatures of CE/EP systems

Sample	T_5 %/°C ^a	T_m /°C ^b	ΔW_{800} °C/% ^c
CE	431	438	42
EP/CE 30/70	408	400	63
EP/CE 50/50	391	390	69
EP/CE 70/30	368	390	71
EP	380	380	84

^a T_5 % is defined as the temperature at 5 % mass loss occurred

^b T_m is defined as the temperature at the main maximum mass loss from the TG curve

^c ΔW_{800} °C is defined as the percent mass loss at 800 °C from the TG curve

basis of the DMTA measurements, that in the case of cyanate/epoxy co-polymers, decrease in T_g as a result of thermal treatment in 250 °C was observed.

Dynamic mechanical analysis of modified systems

The temperature dependence of the storage modulus and loss factor for cyanate and epoxy/cyanate (30/70) matrices modified with polysiloxane and butadiene–acrylonitrile rubbers, which were applied to additionally reduce the crosslink density and improve the impact properties of studied thermosets, are presented in Figs. 8 and 9.

Decrease in the modulus as a result of modification is observed throughout the whole glassy region, which indicates an increase in flexibility of the polymer matrix. The decrease in the loss tangent magnitude in the case of CE and EP/CE systems modified with ETBN seems to be a result of restricted molecular mobility related to the presence of long chain of modifier. The loss factor versus temperature curves for polysiloxane modified samples of CE and EP/CE at the whole temperature range look like those for the systems without PS modifier.

Table 3 Viscoelastic properties obtained for different CE/EP mixtures post-cured at 220 °C

Sample	E'_{20} /MPa	T_g /°C	$\tan \delta$	$S_{1/2}$ /K	$A_{\tan \delta}$ /K
CE	2.368	285	0.44	48	7.1
EP/CE (10/90)	2.440	258	0.42	38	5.7
EP/CE (20/80)	1.836	248	0.40	30	4.8
EP/CE (30/70)	2.219	258	0.43	32	4.8
EP/CE (40/60)	2.182	237	0.39	32	4.3
EP/CE (50/50)	2.355	241	0.40	32	4.6
EP/CE (70/30)	2.116	224	0.32	40	4.8

$S_{1/2}$ $\tan \delta$ peak width at half of peak height, $A_{\tan \delta}$ area under $\tan \delta$ peak

Fig. 8 Storage modulus and loss factor vs. temperature as a result of modification cyanate resin post-cured at 220, 1 CE, 2 +PS (10 wt%), 3 +ETBN (10 wt%)

Fig. 9 Storage modulus and loss factor vs. temperature as a result of modification cyanate resin post-cured at 220, 1 CE/EP, 2 +PS (10 wt%), 3 +ETBN (10 wt%)

Microscopic study

Microscopic characterizations were carried out using SEM analysis of fracture surfaces of samples from Charpy impact tests. SEM fractographs of specimens partly reflect some fracture mechanisms. It was possible to determine the degree of dispersion of modifier particles in the polymer

matrix, the size of modifier domains, and interactions at the interface matrix-phase modifier.

Figure 10 shows the fracture surface of the neat cyanate and epoxy/cyanate with fracture steps and rather smooth areas in between, as is typical for brittle fracture. The main deformation micro-mechanism in the case of unmodified crosslinked resin is a plastic shear in the crack area.

The pure CE shows a brittle fracture surface. SEM micrographs of CE blended with EP do not show any distinct separated phase of each component, indicating good miscibility between the blend components. With the addition of EP, the blends have a much rougher fracture surface consisting of a greater number and shorter length of crevices and all-direction crack propagation. Thus, it can be inferred that there will be a greater improvement in the toughness of these blends when compared with neat CE.

Figure 11 shows SEM fractographs of the CE and CE/EP modified with polysiloxane copolymer. In contrast to the pure CE and CE blended with EP, during analysis of SEM results of these systems modified with polysiloxane and ETBN copolymer, the rubber-rich domains separated in the form of spherical area can be found.

The size and range of PS rubber particles' distribution in CE matrix is of the order of 0.1–1 μm , with the majority of the particles having a diameter of 0.4–0.8 μm . As a result of phase separation of polysiloxane in CE/EP matrix, spherical particles with a diameter ranging from 0.1 to 2 μm can be seen; additionally, it can be seen that the size of second phase particles are larger than in cyanate matrix.

An important factor determining the course of phase separation is gelation phenomena. Small sizes of modifier particles of the order of 0.1–5 μm are formed when phase separation begins almost in the gelation area of the resin. The increase in the forming particles of the second phase is hindered and limited by the diffusion barrier that restricts the mobility of the components. If the separation process occurs much earlier, even during the initial mixing of the components, then the times and conditions favor the formation of larger clusters.

Fig. 10 SEM pictures of fracture surface: **a** CE, **b** CE/EP

Fig. 11 SEM pictures of fracture surface: **a** CE with PS, **b** CE/EP with PS

Fig. 12 SEM micrographs of fracture surface **a** CE+ETBN, **b** CE/EP+ETBN

Figure 12 shows SEM fractographs of the CE/EP modified with ETBN copolymer.

Dispersion of the modifier particles consists of spherical regions with a diameter of 0.5–3 μm , while most of the particles have dimensions of 1.4–1.6 μm . Surface of CE/EP copolymer modified with ETBN is more distorted. This may indicate that the fracture of elastomer particles dispersed in a brittle matrix is stretched plastically at the peak of rupture and forms a kind of bridge between the stretched surfaces. Phase of the rubber is strongly linked with the polymer matrix; deformations of the particles produced during bending are visible in the above photographs, but these particles remain in the polymer, stopping cracks and passing them onto other rubber particles.

Conclusions

The cyanate ester and epoxy resins were used to manufacture composition specimens. The specimens were subjected to varying cure cycles to determine the effect the temperature had on the final product. The results of the DMA testing showed that the neat cyanate resin had

better thermal properties, showing a higher glass transition temperature, T_g , than its mixtures with epoxy resin. Results from TG measurements prove that the presence of epoxy resin reduces thermal stability of the cyanate materials containing addition of epoxy. This observation is in agreement with conclusions from DMA measurements. Specimens that were not post-cured showed a dual $\tan \delta$ peak behavior, indicating that the crosslinked network of the constituent polymers had a low crosslink density and was not fully integrated. Although post-curing process resulted in a single glass transition and an intermediate T_g , in most cases of CE/EP, it was found that increasing the post-cure temperature lowered the T_g and modulus slightly. This decrease in T_g and modulus at high post cure temperatures was attributed to thermal degradation and reduction in crosslink density. Modification of both cyanate resin and epoxy-cyanate mixtures with polysiloxane and butadiene–acrylonitrile copolymers does not have any adverse effect on the storage and loss modulus as well as glass transition temperature. The cyanate and cyanate-epoxy systems modified with these two types of elastomeric agents show two-phase morphology.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Hamerton I. Chemistry and technology of cyanate ester resins. Glasgow: Chapman & Hall, Blackie Academic & Professional; 1994.
- Wang J, Liang G, Zhao W, Zhang Z. Viscoelastic, thermal and mechanical properties of dicyclopentadiene bisphenol diyanate ester/epoxy co-polymers. *Polym Bull.* 2006;57:945.
- Crawford AO, Howlin BJ, Cavalli G, Hamerton I. Examining the thermo-mechanical properties of novel cyanate ester blends through empirical measurement and simulation. *React Funct Polym.* 2012;72:596.
- Fang T, Shimp D. Polycyanate esters: science and application. *Prog Polym Sci.* 1995;20:61–118.
- Tao Q, Gan W, Yu Y, Wang M, Tang X, Li S. Viscoelastic effects on the phase separation in thermoplastics modified cyanate ester resin. *Polymer.* 2004;45:3505.
- Lu SH, Zhou ZW, Fang L, Liang GZ, Wang JL. Preparation and properties of cyanate ester modified by epoxy resin and phenolic resin. *J Appl Polym Sci.* 2007;103:3150.
- Pradhan S, Brahmabhatt P, Sudha JD, Unnikrishnan J. Influence of manganese acetyl acetonate on the cure-kinetic parameters of cyanate ester–epoxy blend systems in fusion relevant magnets winding packs. *J Therm Anal Calorim.* 2011;105:301.
- Hwang JW, Cho K, Yoon TH, Park CE. Effects of molecular weight of polysulfone on phase separation behavior for cyanate ester/polysulfone blends. *J Appl Polym Sci.* 2000;77:921.
- Zhan G, Hu S, Yu Y, Li S, Tang X. The study on poly(ether sulfone) modified cyanate ester resin and epoxy resin cocuring blends. *J Appl Polym Sci.* 2009;13:60.
- Takao I, Takao K, Toshiyuki O, Masao T. Modification of cyanate ester resin by soluble polyarylates. *Polym Int.* 2003;52:773.
- Harismendy I, Rio MD, Marieta C, Gavalda J, Gomez CM, Mondragon I. Dicyanate ester-polyetherimide semi-interpenetrating polymer networks. II. Effects of morphology on the fracture toughness and mechanical properties. *J Appl Polym Sci.* 2001;80:2759.
- Liu J, Ding N, Xu R, He Q, Shen J, Hu B. Cyanate ester resin modified by hydroxyl-terminated polybutadiene: morphology, thermal, and mechanical properties. *Polym Eng Sci.* 2011;51:1404.
- Fang Z, Shzai H, Gu A, Feng Y. Effect of bentonite on the structure and mechanical properties of CE/CTBN system. *J Mater Sci.* 2007;42:4603.
- Brahmbhatt P, Unnikrishnan J, Sudha JD, Pradhan S. Cure kinetics studies of cyanate ester and bisphenol-F epoxy blend. *J Appl Polym Sci.* 2012;125:1068.
- Martin MD, Ormaetxea M, Harismendy I, Remiro PM, Mondragon I. Cure chemo-rheology of mixtures based on epoxy resins and ester cyanates. *Eur Polym J.* 1999;35:57.
- Kim K, Robertson RC. Toughening of thermoset polymers by rigid crystalline particles. *J Mater Sci.* 1992;27:161.
- Williams RJJ, Rozenberg BA, Pascault JP. Polymer analysis-polymer physics, reaction-induced phase separation in modified thermosetting polymers. *Adv Polym Sci.* 1997;128:95.
- Szeluga U, Kurzeja L, Galina H. Curing of epoxy/novolac system modified with reactive liquid rubber and carbon filler. *Polym Bull.* 2008;60:555.
- Szeluga U, Kurzeja L, Galina H. Dynamic mechanical properties of epoxy/novolac system modified with reactive liquid rubber and carbon filler. *J Therm Anal Calorim.* 2008;92:813.
- Alessi S, Conduruta D, Pitarresi G, Dispenza C, Spadaro G. Accelerated ageing due to moisture absorption of thermally cured epoxy resin/polyethersulfone blends. Thermal, mechanical and morphological behaviour. *Polym Degrad Stab.* 2011;96:642.
- Mossety-Leszczak B, Galina H, Włodarska M, Szeluga U, Maciejewski H. Anisotropic epoxy networks. *Macromol Symp.* 2010;291–292(1):127.
- Kurzeja L, Szeluga U, Galy J, Sautereau H, Issartel N. Effect of coal on the rheological and mechanical properties of epoxy matrix. *Macromol Symp.* 2003;194(1):169.
- Wang HM, Zhang YC, Zhu LR, Zhang BL, Zhang YY. Curing behavior and kinetics of epoxy resins cured with liquid crystalline curing agent. *J Therm Anal Calorim.* 2012;107:1205.
- Ciecierska E, Boczkowska A, Kurzydłowski KJ, Rosca JD, Hoa SV. The effect of carbon nanotubes on epoxy matrix nanocomposites. *J Therm Anal Calorim.* 2012. doi:10.1007/s10973-012-2506-0.
- Szeluga U, Moryc P. Curing of dicyanate ester/epoxy copolymers modified with polysiloxane and butadiene–acrylonitrile rubbers. *J Therm Anal Calorim.* 2012;109:73.
- Dinakaran K, Alagar M. Preparation and characterisation of cyanate ester-epoxy interpenetrating matrices/organoclay nanocomposites. *Polym Adv Technol.* 2003;14(8):574.