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Shape memory effect on the formation of oxazoline and triazine rings of BCC/DGEBA copolymer Mathivathanan Ariraman, Ramachandran Sasi kumar and Muthukaruppan Alagar*

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Graphical abstract



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Abstract

The shape memory polymer was developed by the copolymerization of varying weight percentages (30, 40 and 50 wt%) of 1, 3-bis (4-cyanatobenzyl) cyclohexane cyanate ester (BCC) and diglycidyl ether of bisphenol A through the formation of oxazoline and triazine ring without using any external flexibilizer/plasticizer. The copolymer samples were characterized by FTIR spectroscopy, TGA, UV-Vis and XPS analysis. Thermo-mechanical and rheological characterizations were carried out using dynamic mechanical analyzer (DMA). The changes of shape memory behavior and storage modulus were tuned by changing the concentration of oxazoline and triazine ring in the resulting copolymer using varying weight percentages of BCC. The shape fixity behavior increases with increase in weight percentages of BCC up to 50 wt% and beyond this weight percentage of BCC the brittleness behavior of the polymer was noticed.

Key words: Shape memory polymer, copolymer, cyanate ester, DGEBA epoxy

1. Introduction

In the last century, shape memory alloys and polymers had become important class of materials in the area of material chemistry because of their versatile applications in biomedical, aerospace, electronics, etc.,¹⁻⁶. Shape memory polymers (SMP) are of special interest in the field of polymers, since they regain its original shape after the removal of external stimuli including heat, light, solvents, electricity and magnetic fields^{7,8}. The carbon black and carbon nanotube based hybrid SMPs have significant heat absorbance property. Besides, azobenzenes, triphenylmethane leuco derivatives and cinnamates are act as a light sensitive SMPs³. SMPs play a significant role in industrial and academic research areas due to their cost effectiveness, superior shape recoverability and lower density⁹. In addition, the thermo responsive SMPs are

gaining attention due to their amenable processing behaviors with wide range of transition temperatures¹⁰.

Recently, number of SMPs based on polyurethane¹¹, PMMA¹², poly(caprolactone)^{13,14}, PNIPAAm¹⁵, carbon nanotubes-polyurethane were developed¹⁶. Lower cross linked polymers possess lower shape fixity; hence, increasing the cross link density of the shape memory polymer is an important in this field. Accordingly, Wang Kun et al reported that the cross link density of the polymer with effective shape memory effect has been increased by react the cyanate ester with epoxies to obtain hybrid network⁵. The cyanate ester resins are considered as an important material in the field of high performance materials¹⁷. The high thermal stability, superior mechanical strength and high performance widen their applications in printed circuit boards, rocket, missile structures, thermonuclear fusion reactor and high-energy radiation¹⁷⁻²¹. In addition, they also find specialized applications in the areas like low moisture permeable space craft materials due to their cyclotrimerization of cyanate ester monomers (-OCN) like polycyanurate networks.

Epoxy polymers are widely used in the field of adhesives, sealants and coating application^{22,23} but their thermal and mechanical properties are inferior when compared with those of cyanate ester polymers. However there are some aliphatic epoxies and aliphatic diamine curatives which increase the shape memory effect of the polymer composition²². The aliphatic groups present in the epoxy terminal plays a vital role in enhancing the flexibility of the polymer²⁴ by losing their thermal properties resulting in low glass transition temperature, thermal stability and also thermo mechanical properties²².

Hence to overcome such inferior thermo-mechanical properties, in the present work, an attempt has been made to develop thermally stable BCC/DGEBA copolymer by exploiting the concept of shape memory effect. The structurally modified cyclohexyl bridged cyanate ester (BCC) was synthesized and subsequently varying weight percentage of BCC were reinforced into the DGEBA to form BCC/DGEBA copolymer. Then the thermo-mechanical and shape memory behaviors of copolymers were characterized, discussed and reported.

2. Experimental

2.1. Materials

Analytical grade 4-hydroxybenzaldehyde, cyclohexanone, cyanogen bromide (CNBr), triethylamine (TEA), acetic acid, sulfuric acid and solvents were purchased from SRL, India.

DGEBA and 10% Pd/C were purchased from javanthee enterprises and Sigma-Aldrich and were used as received without further purification.



Scheme 1. Synthesis of BCC cyanate ester monomer.

2.2 Synthesis of 1, 3-bis(4-cyanatobenzyl) cyclohexane (BCC)

The precursor 1, 3-bis (4-cyanatobenzyl) cyclohexane (BCC) was synthesized as the previously reported procedure¹⁸. Three steps were involved the synthesis of BCC, (i) BHC (2,6-bis(4-hydroxybenzylidene)cyclohexanone) was synthesized from cyclohexanone and 4-hydroxybenzaldehyde (ii) BHC was reduced to form cyclohexyl branched aliphatic chain bridged phenolic diol (4, 4'-(cyclohexane-1,3-diylbis(methylene))diphenol (CDD) (iii) CDD was dissolved in dry acetone under nitrogen atmosphere, subsequently the solution of cyanogen bromide in acetone was added, followed by the slow addition of triethyl amine at -15 °C. Then the reaction temperature was slowly raised to room temperature and stirred for 1h. The progress of the reaction was monitored by TLC and after the completion of reaction (monitored by TLC), the resulting product was filtered and the filtrate was quenched with cold water to obtain the final product which was washed with water for several times and further dried for 12h at 40°C to yield 88% pale yellow solid as a product.

2.3. Synthesis of BCC/DGEBA copolymer sample

The BCC/DGEBA copolymer with different weight percentages of BCC [30 (0.01 mol), 40 (0.02 mol), and 50 (0.03 mol) wt%] were prepared as follows (Scheme 2); to the solution of

DGEBA in DMF, the BCC was added and stirred for 15 minutes at 30 $^{\circ}$ C to obtain a clear solution. The resulting viscous solution was poured into a respective glass mold and allowed to evaporate the solvent at 50 $^{\circ}$ C for 3h and then the temperature was raised slowly to 210 $^{\circ}$ C at the heating rate of 20 $^{\circ}$ C /h. After that the cured films were removed and preserved for further characterization.

2.4. Characterization

FTIR spectroscopic technique was used to confirm the functional group present in the monomer and copolymer, analysis of samples were carried out by Bruker (TENSOR 27) using KBr pellet method. Thermogravimetric analyses of copolymers were measured using Q500 Hi-Res thermo gravimetric analyzer (TGA). The samples (about 10 mg) were heated from ambient temperature to 750 °C under continuous flow of nitrogen (20 mL/min), at a heating rate of 10 °C/min. Surface morphology of copolymer were studied from scanning electron microscope (SEM) measurements were performed using VEGA 3 TESCAN scanning electron microscope. The piece of a film fixed in the surface of double-sided adhesive tape and the film was sputtered with gold prior to SEM images are observation. Transparences behaviors of the samples were characterized by shimadzu UV-2450 UV–visible spectrometer. The optical images were observed using a Euromex polarized optical microscopy (POM) equipped with a Linkem HFS91 heating stage with a TP-93 temperature programmer and photographs were taken Nikon Coolpix 4500 camera. Samples were placed in between two thin glass cover slips and melted with heating at the rate of 2 °C/min⁻¹.

Dynamic mechanical analyses (DMA) of the copolymer samples were performed with model Q-800 TA Instruments to study their viscoelastic properties. The copolymer samples were cut into 20 mm X 5 mm X 1 mm dimension and then clamped on to the tension clamp of the instrument and scanned from 30 °C to 200 °C at a scanning rate of 3 °C/min. The loss modulus (E") and tan δ values were recorded at a constant linear frequency of 1 Hz and preload force of 0.01 N. The Binding energy were measured using X-ray photoelectron spectroscopic (XPS),the analysis were carried out using a JEOL JPS-9200 photoelectron spectrometer with a monochromatized Al-K α X-ray source operated at 12 kV and 20 mA.



Scheme 2. Polymerization process of BCC/DGEBA

3. Results and discussion

The molecular structures of synthesized monomer were confirmed by FTIR and NMR spectral analysis¹⁸. The varying weight percentages of BCC were copolymerized with DGEBA through the formation of oxazoline ring which were confirmed by FTIR spectra. Fig. 1 shows the disappearance of band at 2263 cm⁻¹ associated with the OCN group of cyanate ester and the appearance of oxazoline ring peak at 1618 cm⁻¹ infers the presences of oxazoline ring and in turn confirms the successful incorporation of BCC into DGEBA. Further it also confirms the oxazoline ring formation through covalent bonding between OCN group of cyanate ester and glycidyl group of DGEBA. The incorporation of 50 wt% of BCC that is beyond the optimum percentage level a new absorption peak corresponding to the triazine ring was observed at 1357 cm⁻¹ due to the self-polymerization of cyanate ester and further the peak intensity increases with an increase in the weight percentage of BCC cyanate ester¹⁸.



Fig. 1 FTIR spectra of BCC/DGEBA copolymer.

XPS spectrum (Fig. 2) was used to confirm the various types of bonds present in the cured copolymer. The overall survey spectrum of 50 wt% BCC/DGEBA copolymer shows the binding energies related to C1s, O1s, and N1s elemental peaks at 284.5 eV, 535 eV, and 401 eV respectively. Fig. 2b and c represent the deconvolution peaks and the corresponding binding energies of C-C, C=C, C-N and N=C-O which coincides with the earlier reports¹⁸. Fig. 2b shows the deconvolution of C1s signal; the major peak at 283.9 eV corresponds to C-C and C=C bond, the second major peak at 285.6 eV is associated with the C-C bonds of aliphatic (core cycloaliphatic groups) carbon atoms²⁵. Subsequently, the third peak at 286.1 eV represents N=C-O bonds of the oxazoline ring indicating the successful epoxy and cyanate ester co-reaction and the final peak at 288.1 eV confirm the C-C=N bond formation²⁶. Fig. 2c shows the deconvolution of N1s signal into two peaks; the peak appeared at 402.5 eV was assigned to the presences of C=N-C bonds of triazine ring in the polymer network and the second peak at 399.5 eV corresponds to the formation of C-N bond. From the binding energy it is ascertained that the cyanate esters were both self-polymerized to form polycyanurate and also co-reacted with epoxy resin with the formation of oxazoline ring. FTIR spectrum (Fig. 1) also supports the presence of both triazine and oxazoline rings in the copolymer system. The data resulted from FTIR and XPS confirms the copolymerization of cyanate ester and epoxy resin.

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Fig. 2 XPS spectra of 50 wt% BCC /DGEBA copolymer a) over all survey spectrum b) C1s deconvolution spectrum and c) N1s deconvolution spectrum

stability of **BCC/DGEBA** copolymers Thermal has been ascertained by thermogravimetric analysis (TGA). Fig. 3 shows the TGA curve of different weight percentages of BCC/DGEBA copolymer. It is clear that the thermal stability of the resulting copolymer increases with increasing weight percentages of BCC. The maximum of 50 wt% BCC/DGEBA copolymer composition exhibits better thermal stability than that of DGEBA/30 wt% BCC copolymer and this may be due to the existence higher amount of rigid triazine ring. In detail, the initial weight loss occurred below 200 °C is probably due to the removal of residual solvent and adsorbed moisture. The major weight loss observed above 300 °C is associated with the decomposition of polymer network and finally yield a residual chair at 750 °C and the data obtained are presented Table 1. Moreover, the higher decomposition temperature and the higher char yield indicate the higher thermal stability of the copolymer. In addition, the combination of higher concentration of oxazoline ring and aliphatic chain significantly lowers the value of Tg which contributes to modify the shape of the polymer at lower temperature (Fig .5). Where as that of higher concentration of triazine ring significantly increases the value of Tg and resist the

modification of shape of the polymer matrix, due to the brittle behaviors of the of a polymer even at higher temperature.



Fig. 3 TGA thermograms for BCC/DGEBA cyanate ester.

DMA was used to investigate the visco-elastic properties of BCC/DGEBA copolymer. Fig. 4a and 4b shows the storage modulus and loss tangent (tan δ) curves for different compositions of BCC/DGEBA with respect to temperature. From the Fig. 4a it is evident that the storage modulus decreased rapidly when the polymer is heated through the switching transition regime and this decrease enabled by the mobility of segments within the polymer thereby inducing the shape memory actuation. The transition temperature (T_{trans}) can be seen in Fig. 4b as the temperature at the maximum value of tan δ . The shape fixity of a material mainly depends on the glassy state modulus (E_g), high E_g provides higher shape fixity²⁷. High glassy state modulus of a material indicates the existences of high cohesive energy which is mostly due to the presence of highly cross linked network structures which leads to minimized propensity for creep related shape change. High glassy modulus is not always mandatory for high shape fixity of the polymer but it is desirable, whereas the higher rubbery modulus (E_r) implies high elastic recovery at high temperature.



Fig. 4 Thermo mechanical property of the BCC/DGEBA copolymer.

The formation of chemical structures of the components significantly contributes to the shape memory properties of the polymers and it is very clear from the data obtained that the concentration of BCC plays an important role as a switching segment in the shape memory copolymers. Among the various weight percentages of BCC, 50 wt% of BCC incorporated DGEBA possesses excellent shape memory behavior with good thermo-mechanical properties. Hence, the formation of oxazoline ring between BCC and DGEBA plays crucial role towards the contribution to the shape memory behavior of a polymer in two ways. Firstly the existence of higher concentration of oxazoline ring significantly reduces the cross link density (Table 1) of the polymers which were calculated using the equation.1,^{28, 29}

$$v_e = E'/3RT$$
----- (1)

Where, v_e = Cross link density, E' = Storage modulus, R = Gas constant and T = Temperature.

Samples	Cross link density	Storage	Char	Glass transition
	$v_e \times 10^{-4} (mol m^{-3})$	modulus	yield at	temperature
	@ T _g +40 °C	(MPa) at 30 °C	750 °C	(°C)
DGEBA/30 wt% BCC	5.0	2743±3	6.65	110
DGEBA/40 wt% BCC	7.4	4586±3	11.87	135
DGEBA/50 wt% BCC	11.3	6262±3	14.77	145

Table.1 Thermal and mechanical property of BCC/DGEBA copolymers

Secondly, the increasing weight percentages of BCC in DGEBA polymer significantly increases the self polymerization of cyanate esters to form triazine ring which in turn increases the cross link density of the copolymer which also contributes to the shape fixity behaviors of the copolymer. The storage modulus and glass transition temperature of the copolymers are increased with increasing the concentrations of BCC from 30 to 50 wt% which are listed in Table 2. Despite the fact that the 50 wt% BCC/DGEBA possesses excellent shape fixity properties with enhanced thermal stability the 50 wt% of BCC reinforced DGEBA also possess high rigidity improved strength behaviors due to the formation of higher concentration of polycyanurate network.



Fig. 5 Bending test of 50 wt% BCC/DGEBA copolymer.

 Table 2. Elastic modulus ratio, Loss tangent and shape memory properties of BCC/DGEBA copolymers

Samples	E _g /E _r	T _{trans} °C	% shape recovery T _{trans} +20°C	% shape fixity T _{trans} -10 °C
DGEBA/30 wt% BCC	66	115	95	90
DGEBA/40 wt% BCC	45	140	96	96
DGEBA/50 wt% BCC	42	150	98	100



Fig. 6 50 wt% BCC/DGEBA copolymer reversibility of T_{switch} during the heating and cooling cycles (heating-cooling range: 60-200°C, heating rate: 3 °C/min).

Bending test was carried out to determine the shape memory behavior of the copolymer samples between the temperatures ($T_{trans}+25$) and ($T_{trans}-10$). The shape changes were made with respect to the glass transition temperature. 50 wt% BCC/DGEBA was used to demonstrate the shape memory behavior as changing the temperature of the copolymer as shown in Fig. 5. The original rectangular planar shape (a) was heated at $T_{trans}+25$ and the sample was immediately deformed into different shapes through bending and twisting, upon cooling under load, these deformed temporary shapes (b) were fixed, the shape was retained until the material was heated to higher temperature³⁰. The sample recovered its original rectangular shape (c) on reheating at

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above T_{trans} . The recovered shape was indistinguishable from the original shape, confirming the excellent shape fixity and recovery. The shape recovery time was noted at various temperatures, and the original shape was obtained at above the T_g value. The percentage of shape recovery and retention are calculated using equations 2 and 3¹⁰.

Shape recovery (%) =
$$[\theta_{max} - \theta_i/\theta_{max}] * 100$$
------(2)
Shape retention (%) = $(\theta_{fixed} - \theta_{max}) * 100$ ------(3)

The polymer was heated to a temperature $T_{trans} + 25$ °C and deformed to an angle (θ_{max}) . Then the deformed polymer was cooled to T_{trans} -10 °C to fix the deformation and the resultant deformation was measured by angle (θ_{fixed}) . Then the deformed polymer was reheated to $T_{trans}+25$ °C and the change in angle (θ_i) was recorded¹⁰.

The SMP is heated to a deformation temperature (T_d) (above Tg temperature), which leads to the material soft and flexible. After applying a force deformation was noted (i.e. loading). Then decreasing the temperature (below Tg) under the same loading condition, upon unloading the force, the deformed temporary shape is fixed, which marks the completion of the shape fixing². The shape recovery time varies with varying weight percentages of BCC and this indicates the contribution of formation of chemical structures. 50 wt% of BCC reinforced DGEBA has 98% shape recovery at 120 sec with 100% shape fixity. The percentages of recovery have been determined by reheating the samples gradually with increasing the temperature and the deformation was measured at different temperatures as shown in Fig. 4. 30 wt% and 50 wt% recovery were obtained at 115 °C and 150 °C respectively. When the sample was attaining at T_{switch} (175 °C), 98% recovery was obtained and above the T_{switch} (T_{trans}+25) 100% recovery of sample was obtained. In addition, the presence of aliphatic chain^{10, 27}in the cyanate ester (BCC) significantly contributes to the effect of the shape memory behaviors of copolymers. Moreover, the shape recovery time was mainly influenced by the presence of higher concentration of triazine ring because of the crosslink density which significantly hindered the segmental chain mobility in copolymer matrix. The switching temperature (T_{switch}) during the heating process was observed at 145 °C. T_{switch} during cooling process strongly induces the delay in reorganization of segment. The reproducibility (Fig. 6) in repeated cycle shows that the system regains its shape memorizing capability on the heating-cooling cycle²³.

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Fig. 7 DRS-Vis spectrum of BCC/DGEBA copolymers

Transparent behavior of BCC/DGEBA polymers is shown in Fig. 7. On increasing the BCC concentration, the transparent behaviors of the polymer was decreased due to the formation of triazine by cyanate ester. Mostly the cyanate ester based polymers are used in space applications because of their radiation resistance, but it was limited due to their poor transparency^{19,20,31}. On the other hand, epoxy polymers possess limited radiation resistance with good transparent behaviors^{19,20,32}. Hence, when epoxy and cyanate ester monomers were copolymerized, the synergistic properties of epoxy and cyanate ester together improve the radiation resistance and transparency of the polymer to a significant extent. 30 wt% BCC incorporation BCC/DGEBA copolymer exhibits 73.6% @ 800 nm transparences behaviors where as that 50 wt% BCC possess 66.2% @800 nm due to the influencing effect of epoxy compound in the copolymer.

4. Conclusions

With a view to develop the shape memory polymer, cyanate ester based thermosetting polymer was synthesized by the copolymerization of BCC and DGEBA. The different weight percentages of BCC/DGEBA were developed and their thermo-mechanical and shape memory properties were examined. It was inferred that the formation of oxazoline and triazine rings play

a key role in the storage modulus and shape fixity behavior. A shape memory polymer is developed through the reaction between BCC and DGEBA where, the oxazoline ring formation is influenced by the BCC monomer in the copolymer system and in addition to this, they also undergo a self polymerization to form triazine ring thereby increasing the crosslink density of the copolymer. Higher loading beyond 50 wt% of cyanate ester increases the brittleness and reduces the transparent behaviors of the copolymer. 50 wt% BCC/DGEBA copolymer have better shape memory behavior with higher shape fixity, higher storage modulus, better shape recovery with improved thermal stability.

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