LIPS International Journal of Interdisciplinary Research Volume 1, Issue 2, October 2024 - SPECIAL ISSUE
Proceedings ISBN 978-93-94174-47-4 “International Conference on interdisciplinary research, education and job scope”

Comparative Study of Shape Memory Bisphenol A and Bisphenol F Cyanate Ester Systems

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A shape memory polymeric precursor *viz:* phenol telechelic poly(ε-caprolactone) synthesized by reacting *para*-hydroxyl benzoic acid with poly(ε-caprolactone) diol (PCL). The polymer was characterized by FTIR, ester value and SEC. The novel thermoset polymers showing shape memory properties were synthesized by reacting diglycidyl ether of bisphenol A (DGEBA) and phenol telechelic poly(ε-caprolactone) (PCLOH) with different cyanate ester resins such as bisphenol A cyanate ester (BACE) and bisphenol F cyanate ester (BFCE). The cure characteristics of the blend were evaluated by FTIR, DSC and SEM. The blend with fixed proportion of epoxy, PCLOH and different cyanate esters were studied for their flexural, dynamic mechanical, thermal properties and shape memory properties. These epoxy-cyanate ester systems possess good thermal, mechanical and shape memory characteristics for potential use in smart actuator development. The advantage of this system includes controllable transition temperature and good processability than traditional shape memory thermoset system.

Keywords: Shape memory polymers; Cyanate ester; Poly(ε-caprolactone); Smart actuator.

Introduction

The demand for shape memory polymers in both earth and space application fields is increase in recent years as the technologies move towards smart systems. Thermo-responsive shape memory polymers find potential applications particularly in space and biomedical applications [1-3]. Literature cites the development of a host of polymers belonging to the class of thermoplastics and a few thermosets exhibiting shape memory characteristics. Among the thermosets, epoxy resins are the most versatile ones in view of their ease of synthesis, umpteen ways of effecting the curing, amenability for copolymerisation, compounding, composite processing etc. In fact, epoxies are the best suited for elastic memory composites with good strength characteristics if they possess shape memory properties [4-6]. Many reports refer to the use of proprietary shape memory epoxy formulations and composites derived thereof, for development of several self-deployable systems for potential space applications [7-10]. However, there are no details on their synthesis or processing aspects or on the structural features leading to the manifestation of shape memory properties. Though epoxy resins are the workhorse matrix for structural composites, it is not the ‘last word’ in thermoset.

Cyanate ester (CE) emerges as a better alternative for epoxies with several advantages as CE is the answer to many issues raised by epoxies for aerospace applications. It forms highly crosslinked, three-dimensional triazine-linked polycyanurate networks through a polycyclotrimerization reaction in the presence of suitable catalysts. The properties of cyanate ester can be modified by reaction with an epoxy resin. The moisture resistance of CE is increased, whereas the thermal properties are not obviously sacrificed, when epoxy is introduced [11]. The toughness of CE/epoxy system depends on the molar ratio of CE to epoxy.

Xie et al. studied the shape memory properties of epoxy resins and aliphatic amine. They tuned glass transition temperatures of epoxy resins by varying the crosslink density of the systems [12]. Merline et al. synthesized shape memory oxazolidinone polymer by reacting isocyanate with hydroxy-telechelic poly(tetramethylene oxide) and an epoxy resin. The modulus ratio and shape recovery increased with increase in the oxazolidinone-content in the polymer [13]. Tong et al. reported the shape memory cyanate ester synthesized from polyols and diols in presence of metal catalyst. The obtained glass transition temperature was greater than 150 °C [14].

The present work is mainly focused on the synthesis, characterization and shape memory properties of thermoset epoxy- cyanate esters systems. The research includes detailed investigations on the synthesis of selected shape memory thermoset polymers *viz*: epoxies and cyanate esters. An attempt has been made to correlate the shape memory behavior to the structural features and morphology of the systems. It is hoped that the findings of this study make modest contributions to the emerging field of shape memory materials which have tremendous application potential in many areas especially where manual intervention is impossible as in the case of space exploration and planetary mission.

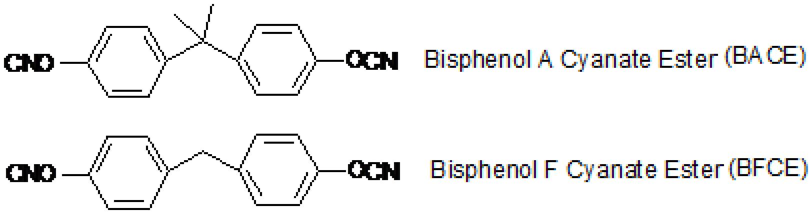
EXPERIMENTAL

Synthesis of phenol-functional oligomers (PCLOH)

PCLOH was synthesized by reaction of PCL diol (0.1 mol) with PHBA (0.6 mol) in toluene/diglyme solvent in the presence of pTSA as catalyst. The mixture was refluxed for 20 *h* and the byproduct water was removed by azeotropic distillation using toluene in a Dean Stark apparatus. After completion of reaction, the solvent was removed by distillation and the resultant viscous fluid was poured into $CHCl_3$ and the unreacted PHBA was filtered out. The filtrate was washed several times with 5% $NaHCO_3$ solution to remove the catalyst and unreacted PHBA. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4, for one day, filtered and the solvent was removed in a flash evaporator at 60 °C. The resultant resin was characterized by fourier transform infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). Estimation of ester value was done by chemical analysis.

Synthesis of shape memory epoxy-cyanate ester resin

The DGEBA/PCLOH/BACE blend and catalyst (zinc octate and nonyl phenol, 4 wt% of BACE) were first mixed together, degassed at 80 °C for 30 min and then poured into a steel mould. Blends with bisphenol F cyanate ester (BFCE) of DGEBA and PCLOH were prepared using same procedure. Composition of DGEBA/PCLOH/DCE (different cyanate ester), molar ratio-1/0.07/0.82 was selected in this study. Since three components of the base resins systems are difunctional and have same molar mass, their molar ratios equal their equivalent ratios. Structure of various cyanate esters is shown in scheme 1.



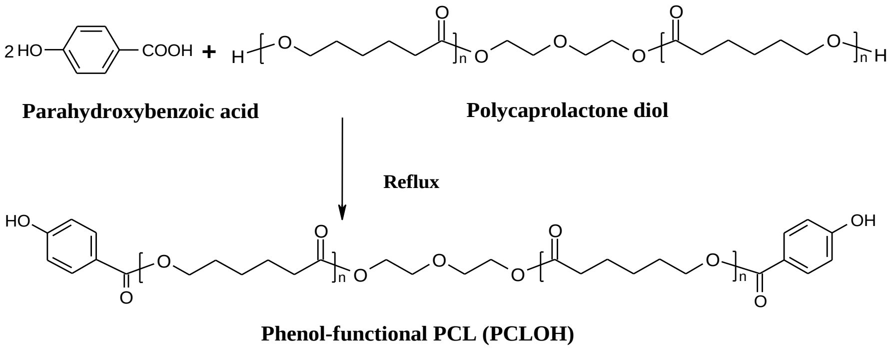
Scheme 1 Structure of different cyanate ester

RESULTS AND DISCUSSION

Synthesis and characterization of PCLOH

The method of synthesis of PCLOH is illustrated in scheme 2 and FTIR spectra of PCLOH are shown in Fig. 1. The peak at 3403 cm^{-1} corresponds to stretching vibration of -OH groups and that at 1724 cm^{-1} to the C=O stretching of the ester group. The peak at 1164 cm^{-1} corresponds to C-O-C stretching of PCLOH. The polymer was further characterized by ester value estimation.

The ester value of PCLOH (47 mgKOH/g) conformed nearly to the theoretical value (50 mgKOH/g). The similarity in SEC profiles by both refractive index and UV detector techniques shows that all polymer chains are end-capped with phenolic groups (Fig. 2). PCL diol is insensitive to UV detector as it doesn’t contain any chromophoric groups. On end-capping with phenol group, it becomes a UV sensitive. The similarity in SEC profiles by both refractive index and UV detector technique shows that all polymer chain ends are end-capped with phenolic groups.



Scheme 2 Synthesis of PCLOH

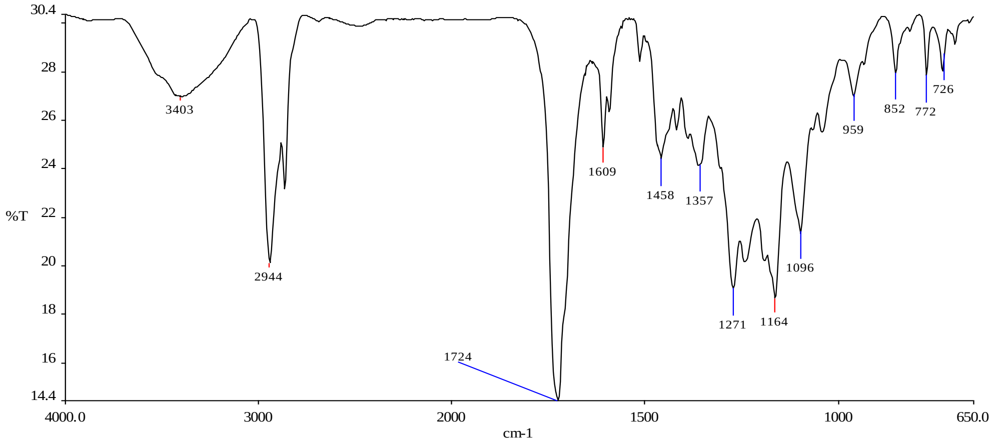


Fig. 1 FTIR spectrum of PCLOH

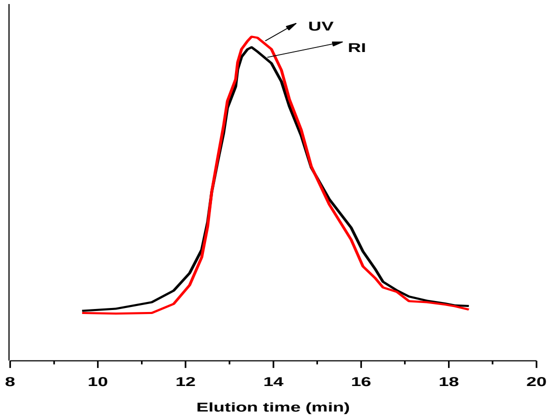
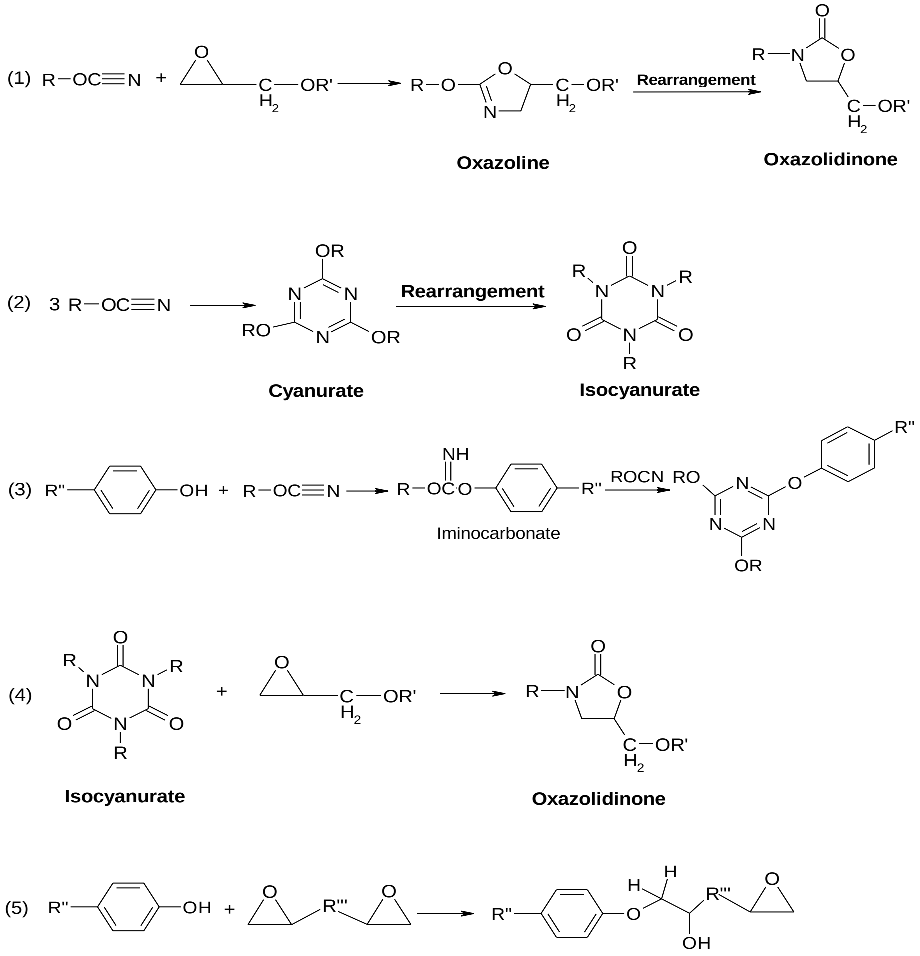


Fig. 2 SEC profiles of PCLOH (Superimposition of RI and UV detected traces).

Cure characterization of epoxy-cyanate ester system using different cyanate ester

The cure schedule of the DGEBA/PCLOH/BACE (PCLBA) and DGEBA/PCLOH/BFCE (PCLBF) blends were determined by DSC and FTIR. The DSC profiles (Fig. 3) of PCLBF system shows one exotherms at low temperature and the other at higher temperature (Table 1). The exotherm at 175 °C is attributed to cyanate-epoxy reaction leading to the formation of oxazolidinone groups (Scheme 3, pathways 1 and 4) [15] and that at 185 °C to the polymerisation of cyanate groups (Scheme 3, pathway 2) [14, 15]. In PCLBA system shows one exotherm (Fig. 3) at 185 °C, due to the formation of triazine network.



Scheme 3 The likely reaction pathways of the curing process

From FTIR, (Fig. 4) completion of cure reaction of the epoxy and –OCN groups of three systems (PCLBA and PCLBF) in the network was confirmed from the absence of peaks corresponding to epoxy ring at 916 cm^{-1} and of –OCN at 2271-2238 cm^{-1}. It was further confirmed from the appearance of triazine peaks at 1363 cm^{-1} and absorptions of isocyanurate at 1698 and 1459 cm^{-1} [16, 17]. The oxazolidinone rings formed from the reaction of cyanate and epoxy was observed at 1731 cm^{-1} [14]. Following the above studies, all the compositions were cured under same cure schedules: 100°C - ½ *h*, 120 °C-1 *h*, 150 °C-1*h*, 180 °C-1 *h* and 200 °C-3 *h*.

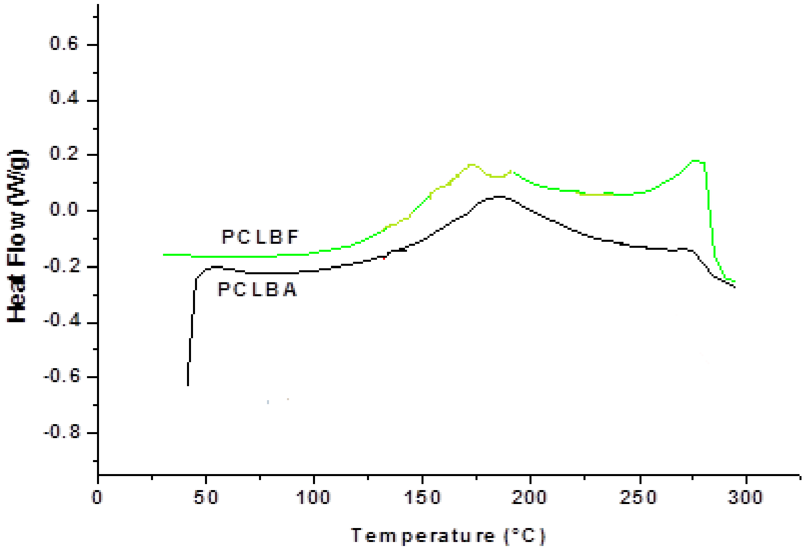


Fig. 3 DSC profile of different systems

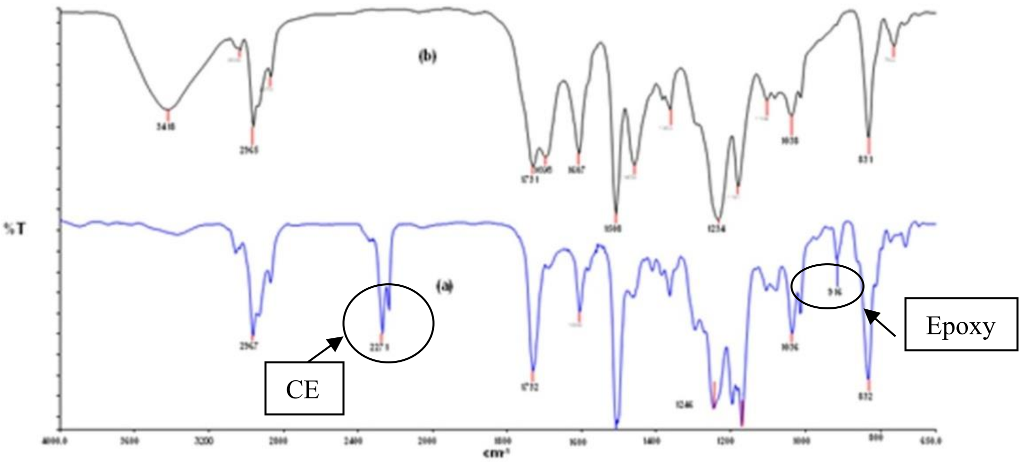
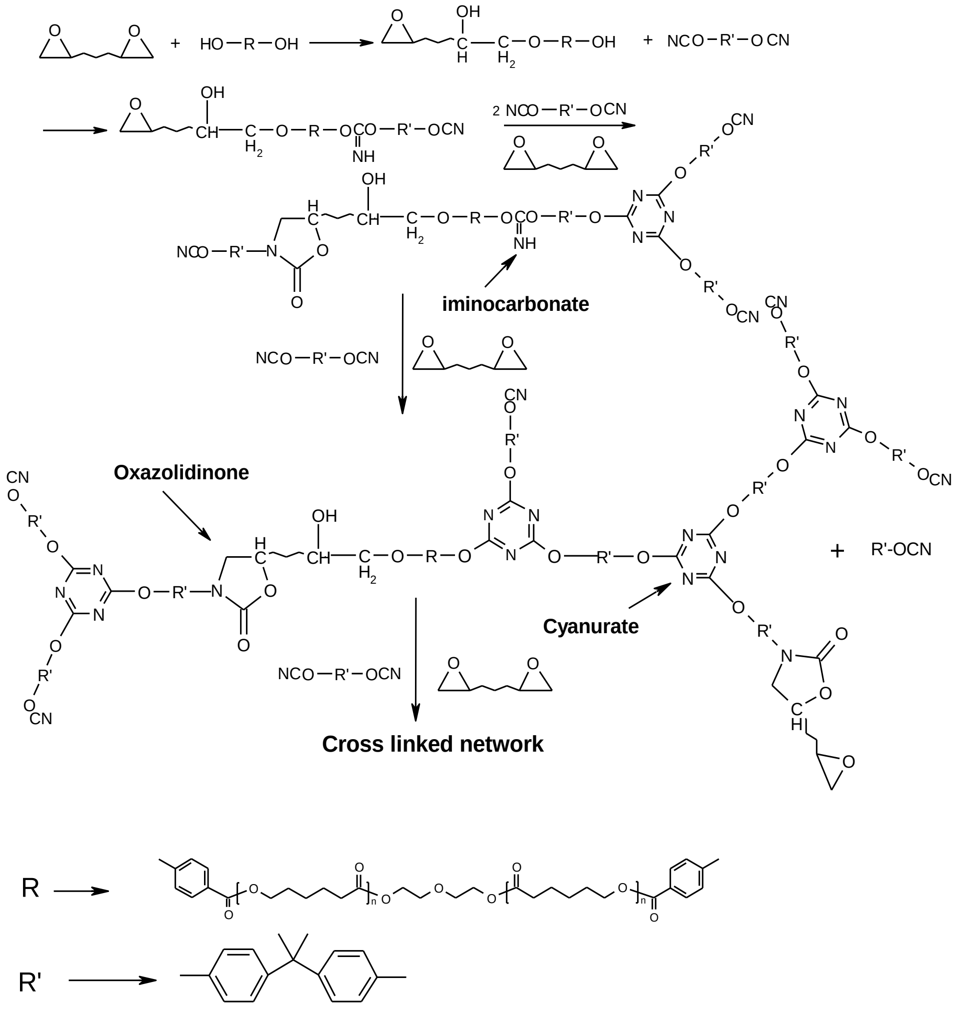


Fig. 4 FTIR Spectra of PCLBA (a) uncured and (b) cured blend (200 °C, 3h)

In a recent paper reported that the cyanate ester polymerization in the nonfunctionalized PCL blend occurred at high temperature [18]. The blend containing functionalized PCL showed this exotherm at lower temperature, due to the involvement of the phenolic groups of switching segments in the catalysis of cyanate ester homopolymersation (Scheme 3, pathway 2). It is possible that the phenol groups react with epoxy resin also. The likely mechanisms of co-reaction of epoxy resin with cyanate ester involving the PCLOH are shown in scheme 4.



Scheme 4 Possible reaction mechanism leading to network structure for DGEBA/PCLOH/BACE system.

Table 1 Composition of the ternary blend, DSC exotherm peak maxima of epoxy-cyanate ester systems containing different cyanate ester.

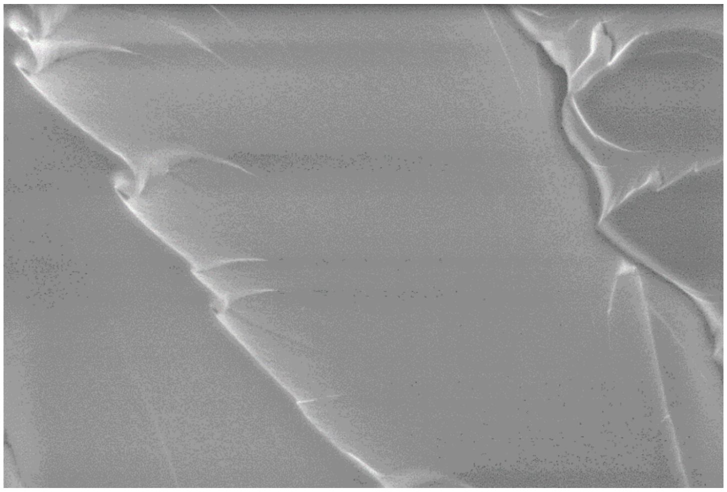
Sample	Molar ratio of DGEBA/SS/BADC	Peak max 1 (°C)	Peak max 2 (°C)
PCLBF	1/0.07/0.82	175	185
PCLBA	“	-	185

Flexural properties of different systems

The PCLBA system shows better flexural strength (Table 2) than PCLBF. The switching segments (PCLOH) are expected to provide the epoxy-cyanate ester more flexibility which could help improve its shape memory property.

Scanning electron microscopy (SEM)

Fig. 5 [(a) and (b)] are the SEM images of the fractured surfaces of PCLBA, and PCLBF. In the case of PCLBA and PCLBF, [Fig. 5 [(a) and (b)], the blends possessed relatively ductile fracture. Compared the SEM images of PCLBA and PCLBF, later shows more brittle pattern. This is due to bisphenol A cyanate ester contain two -CH_3 group, nevertheless these groups are absent in bisphenol F cyanate ester, therefore its crosslink density is higher than PCLBA.



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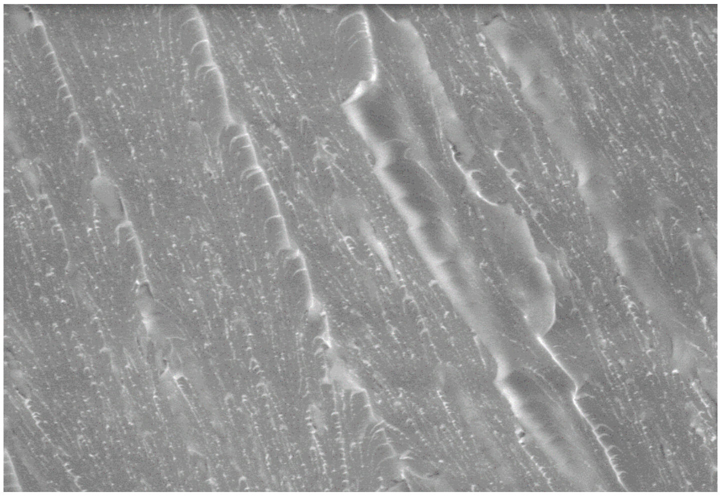

b

Fig. 5 SEM images of the fracture surface of (a) PCLBA and (b) PCLBF.

Thermo gravimetric analysis (TGA)

Fig. 6 represents the typical TGA of the PCLBA. The two systems showed thermal stability above 280 ºC. The cyanate ester-epoxy system alone normally decomposes at temperature >350 ºC. Additions of the shape memory components diminish the thermal stability. The PCL made the system thermally least stable. Practically, all the PCL got degradation at around 300 ºC. However, all the systems have stability well above their service temperature (normally around the transition temperature).

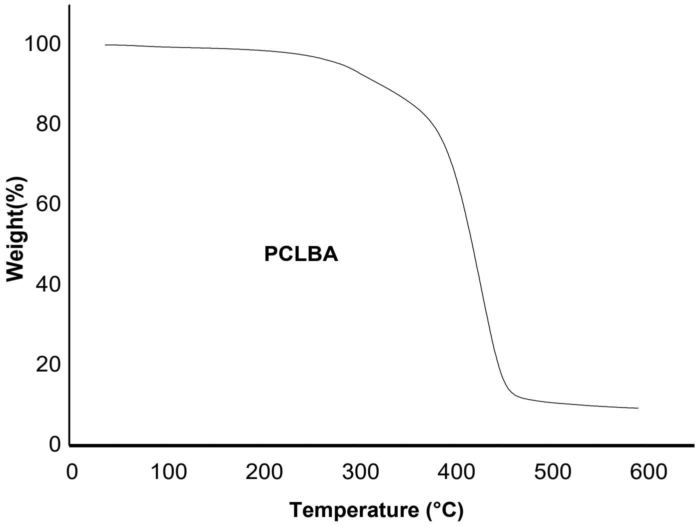

Fig 6 TGA traces of DGEBA/PCLOH/BACE blend (N_2**,** heating rate-10 °C/min).

Dynamic mechanical thermal properties

Visco-elastic properties of the samples were investigated by DMTA in three point bending mode. Fig. 7, indicate the loss tangent ($tan\delta$) for different switching segments as a function of temperature. The transition temperature T_{trans} was determined from the tanδ peak. The modulus ratio E_g/E_r is taken as ($E'_{Ttrans-20}/E'_{Ttrans+20}$). Where, $E'_{Ttrans-20}$ and $E'_{Ttrans+20}$ stand for the storage modulus at temperature $T_{trans-20}$ and $T_{trans+20}$, respectively. Initially, PCLBF show higher storage modulus than PCLBA. While the storage modulus decreases, the E_g/E_r ratio (Table 2) increases in the order PCLBF<PCLBA. The transition temperature shows similar trend of storage modulus in the order PCLBA<PCLBF. The high transition temperature of PCLBF is due to crystalline nature of the segments (absence of $–CH_3$ groups) when compared to PCLBA.

Table 2 Flexural strength, loss tangent, elastic modulus ratio and shape memory properties of different systems

Sample	Flexural strength (MPa)	T_{trans} (°C)	E_g/E_r	% of shape recovery at $T_{trans}+20$ (°C)	Recovery Time (min)	% of shape fixity at $T_{trans}-20$ (°C)
PCLBF	96± 0.5	157.68	12	90	1.35	95
PCLBA	100 ± 0.5	119.08	17	95	1.00	98

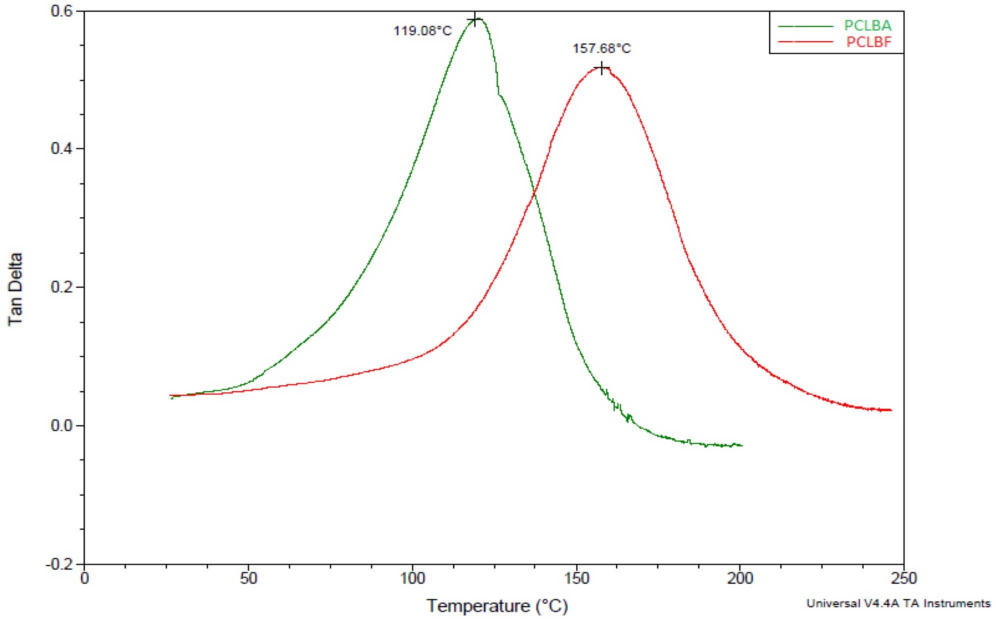

Fig. 7 Loss tangent-temperature profile of PCLBA and PCLBF

Shape memory properties (Bending test)

Qualitatively, the shape memory behavior was estimated by bending test between the temperatures ($T_{trans}+20$ °C) and ($T_{trans}-20$ °C). The shape memory studies are done with respect to the transition temperature. The shape memory behavior of a representative sample, PCLBA is demonstrated in Fig. 8. The original (permanent) rectangular shape (a) was heated at $T_{trans}+20$ °C and the sample was deformed into different shapes through bending and twisting. Upon cooling under load, these deformed temporary shapes (b) were fixed. On reheating above T_{trans} the sample recovered its original rectangular shape (c). The recovered shape was indistinguishable from the original shape, confirming the excellent shape fixity and recovery.

For quantitative evaluation, the bending tests of two systems (PCLBA and PCLBF) were conducted in temperature $T_{trans}+20$ (°C) (Table 2). At $T_{trans}+20$ (°C) the shape recovery increases in the order PCLBF<PCLBA. The observation conforms to the modulus ratio (E_g/E_r). The recovery time decreases proportionally. At high E_g/E_r ratio, the shape recovery is maximum at minimal recovery time.

Fig. 5.8 Shape memory properties of PCLBA (a) original/permanent shapes, (b) fixed temporary shapes and (c) recovered shapes.

On increasing the temperature ($T_{trans}+30$) (°C) the two systems showed good shape recovery, as higher temperature favored the chain relaxations. Though the cyanate ester system showed good thermal and mechanical properties, it exhibited relatively poorer shape memory properties by way of providing a rigid matrix with low concentration of shape memory component. The highly cross-linked structures have strong restraining force on their segments, which need large free volume and more energy, necessarily higher temperature to accomplish shape recovery [19]. The present system possesses shape fixity to the tune 95-98 % and shape recovery of 90-95 %. It is mechanically sturdy and has good thermal stability to be used in composites for developing smart system for diverse application. The advantage of this system includes controllable transition temperature and good processability than traditional shape memory thermoset system.

Conclusions

The novel thermoset polymers showing shape memory properties were synthesized by reacting diglycidyl ether of bisphenol A (DGEBA) and phenol telechelic poly(ε-caprolactone) (PCLOH) with two cyanate ester resins such as bisphenol A cyanate ester and bisphenol F cyanate ester. The SEM analysis of PCLBA and PCLBF, the blends possessed relatively ductile fracture. The TG analysis of all the three systems showed thermal stability above 280 ºC. Initially, PCLBF show higher storage modulus than PCLBA. The E_g/E_r ratio increases in the order PCLBF<PCLBA. The high transition temperature of PCLBF is due to crystalline nature of the segments when compared to PCLBA. The shape recovery and the recovery time of PCLBA system are better than PCLBF. The present system possesses shape fixity to the tune 95-98 % and shape recovery of 90-95 %. The actuation temperature could be tuned by varying the PCLOH content. The polymer possessed good mechanical properties, thermal stability and shape recovery characteristics that could be controlled by varying the composition of the matrix. The resin is suited to process good

elastic memory composites as cyanate esters normally promote excellent composite formation. These systems are potentially useful for fabricating smart systems like actuators.

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