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RESEARCH ARTICLE

Chemically cross-linked poly(a-caprolactone): Synthesis, characterization, and shape memory behavior

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Abstract

Thermoset polymers exhibiting shape memory properties were derived on reacting digycidyl ether of bisphenol A (DGEBA) with bisphenol A dicyanate ester (BADC) in presence of a shape memory polymer precursor i.e. phenol-telechelic poly(ε-caprolactone) (PCLOH) that was synthesized. Cure characteristics of the blends were investigated by differential scanning calorimetry and FTIR. Blends with varying proportions of DGEBA/PCLOH/BADC were studied for their flexural, dynamic mechanical and shape memory properties. The flexural strength and modulus decreased with increase in concentration of poly(ε-caprolactone) (PCL). The storage modulus and the transition temperature (T_{trans}) of the systems also showed a similar trend. These polymers showed good shape memory properties. PCL increased the modulus ratio (*Eg/Er*) which in turn increased the extent of shape recovery with a concomitant diminution in the shape recovery time. An increase in temperature results in faster recovery with an increase in the extent of shape recovery. The epoxy-cyanate ester system possesses adequate thermal, mechanical and shape memory characteristics for possible use in smart actuatorsystems.

Keywords

Polymer
Cyanate ester-epoxy blend
Poly(ε-caprolactone)
Epoxy-cyanate ester

Introduction

Shape memory polymers are stimuli-responsive polymers that possess the ability to change their shape upon application [1, 2] of an external stimulus (*e.g.* temperature, electric or magnetic field, pH). The demand for shape memory polymers in both earth and space application fields is on increase in recent years as the technologies move towards smart systems. Thermo-responsive shape memory polymers find potential applications particularly in space, biomedical applications. 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

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elastic memory composites with good, strength characteristics if they possess shape memory properties. 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. However, there are no details on their synthesis or processing aspects nor 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 can form highly crosslinked, three-dimensional polycyanurate networks through a polycyclotrimerization reaction in presence of suitable catalysts. The moisture resistance increases along with the thermal stability, when epoxy is reacted with CE [3]. The toughness of CE/epoxy system depends on the blend composition.

Apart from the synthesis and characterization of these polymer systems, the research was targeted also to achieve controllable transition temperature and good processability in comparison to reported shape memory polymer systems. The composites with adequate strength are targeted for the development of temperature responsive, self-deployable systems for related applications.

The general strategy for developing any SMP is to incorporate a known SMP component in the matrix of interest preferably by way of copolymerization. *Examples of such components are* poly (tetramethyleneoxide), poly(ε-caprolactone) etc. In this work also, this strategy was followed.

There are a good numbers of reports on shape memory epoxy resin systems [4,5]. It can be seen that majority of them are patented. There are a few reports on cyanate ester based shape memory polymer for space deployable application [6-8]. However, these reports miss the details of achieving shape memory characteristics to the resin system. This blend system has many features better than epoxy and cyanate ester that they provide better mechanical and hygrothermal properties and the desirable low thermal expansion as reported in literature [9] while, maintaining the processability of epoxies. They can form better composites than epoxy resin alone. These qualities render them better candidate as matrices in polymer composites particularly for space applications. This present work reports the synthesis of a shape memory epoxy-cyanate ester resin system based on diglycidyl ether of bisphenol A cured with bisphenolAdicyanate ester (BADC). For the shape memory effect, a component, *viz*: PCLOH was synthesized and co-reacted with the epoxy-cyanate ester system. Thus, DGEBA/PCLOH/BADC blends of different compositions were prepared and evaluated for thermal, mechanical, thermo-mechanical and shape memory properties. This work outlines the compositional dependency on their shape memory properties.

Experimental

Synthesis of PCLOH

PCLOH was synthesized by reaction of hydroxy-telechelicpoly(ε-caprolactone) (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 FTIR and size exclusion chromatography. Estimation of ester value was done by chemical analysis.

Preparation of epoxy-PCLOH-cyanate ester based thermoset system

The DGEBA/PCLOH/BADC blend and catalyst (4 wt% of BADC, Catalyst was prepared by mixing of zinc octate and nonyl phenol in a weight ratio of 3:40) were first mixed together, degassed at 80 °C for 30 min., and then poured into steel mould. Different compositions of DGEBA/PCLOH/BADC were selected in this study. Since the components of the base resins systems are difunctional and have same molar mass, their molar ratios equal their equivalent ratios.

Fold-deploy shape memory test (Bending Test)

The fold-deploy shape memory test includes three steps [10]. A straight rectangular strip of polymer of size 120 x 15 x 2.6 mm was used for the test. For polymer composite its dimension is 120 x15 x 1 mm.

First step is the heating of the sample to 20 °C above its T_{trans} (Transition temperature, T_g+20) and then bending into a "U" shape. The maximum bending angle was measured as θ_{max}. In the second step, the U-shaped sample was cooled (T_g-20) to fix the shape. While fixing, marginal recovery occurred and the bending angle was measured as θ_{fixed}. Then the deformed polymer was reheated (T_g+20) and the residual angle (θ_{final}) was recorded. The shape fixity, R_f, and shape recovery ratio, R_r, were calculated using the following equations. Average of the three measurements is reported

$$\text{Shape recovery (\%)} = [(\theta_{max}-\theta_{final})/\theta_{max}] \text{ x } 100 \quad (1)$$

$$\text{Shape retention (\%)} = [\theta_{fixed}/\theta_{max}]\text{x } 100 \quad (2)$$

Results and discussion

This work reports the synthesis of a shape memory epoxy-cyanate ester resin system based on diglycidyl ether of bisphenolA cured with BADC. For the shape memory effect, a component, *viz*: PCLOH was synthesized and co-reacted with the epoxy-cyanate ester system. The molar ratio of cyanate ester and epoxy resin was maintained as 0.82:1.0. Two compositions containing 20 and 38 weight% of PCLOH were prepared and evaluated for mechanical, thermo-mechanical and shape memory properties. This part outlines the compositional dependency on their shape memory properties.

Synthesis and characterization of phenol functional of different compositions

The method of synthesis of PCLOH is illustrated in **Fig 1.** From FTIR the peak at 3419 cm^{-1} corresponds to vibration of -OH groups and that at 1725 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.

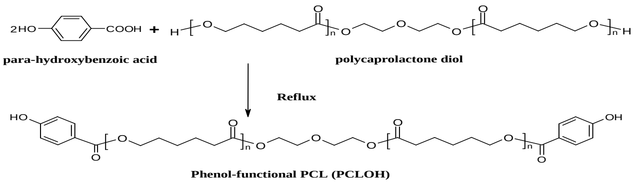

Fig 1 Synthesis of PCLOH

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 PCL segments are insensitive to UV detector, as it doesn't contain any chromophoric groups. On end capping with phenolic group, it becomes a UV sensitive. The similarity in SEC profiles **Fig 2** by both refractive index and UV detector techniques shows that all polymer chain ends are end-capped with phenolic groups.

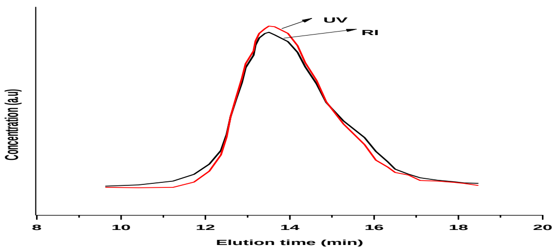

Fig 2 SEC profiles of PCLOH (Superimposition of RI and UV detected traces)

Cure characterization of DGEBA/PCLOH/BADC blends

The cure schedule of the blend was determined by DSC and FTIR. The DSC profiles of the PCL-20 **Fig 3** show two exotherm one at low temperature (170 °C) and other at high temperature (185 °C). The exotherm in the range of 170-185 °C **Table 1** is attributed to cyanate-epoxy reaction leading to the formation of oxazolidinone groups and that at 185 °C to the polymerization of cyanate groups. While the cyanate ester polymerization in the epoxy/cyanate ester alone occurred at high temperature (240 °C) [10] the blend containing (PCL system) showed this exotherm at lower temperature.Due to the involvement of the phenolic groups of PCLOH in the catalysis of cyanate ester homopolymerization. It is possible that the phenol groups react with epoxy resin also. This reaction occurs [11] in the temperature range 180-200 °C (**Fig 4**).

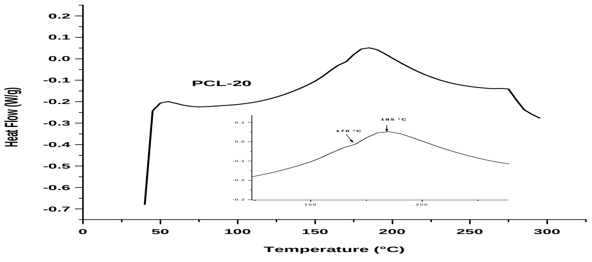

Fig 3 DSC profile of PCLOH.

From FTIR completion of cure reaction of the epoxy and –OCN groups of system in the network was confirmed from the absence of peak corresponding to epoxy ring at 915 cm^{-1} and of – OCN at 2270-2235 cm^{-1}. It was further confirmed from the appearance of triazine peaks at 1560 (peak merge with aromatic peak) and 1363 cm^{-1} and absorptions of isocyanurate **Fig 4** at 1695-1459 cm^{-1}. The oxazolidinone rings **Fig 4** formed from reaction of cyanate ester and epoxy is observed [12] at 1736 cm^{-1}. 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

Similar results were obtained in higher shape memory component containing system (PCL-38) as those obtained in the case of PCL-20 as discussed above. The mechanisms of co-reaction of epoxy resin with cyanate ester involving the PCLOH segments are proposed based on the possible reaction pathways of cyanate ester and epoxy resin, cyanate ester and phenolic group, epoxy and phenolic group as described in literature [13].

Table 1 Composition of the ternary blend, DSC exotherm peak maximum of epoxy-cyanate ester systems for different compositions of blends).

Sample	Molar ratio of DGEBA/PCLOH/ BADC	Mass % of DGEBA/PCLOH /BADC	Peak max1 (°C)	Peak max 2 (°C)
PCL-20	1/0.07/0.82	50/20.5/30.5	170	185
PCL-38	1/0.16/0.82	38.5/37.8/23.6	158	210

Flexural properties

Table 2 compiles the flexural strength and modulus of the various DGEBA/PTOH/BADC systems. The flexural strength and modulus decrease with increase in concentration of PCLOH. The cyanate ester content increases the flexural strength and modulus. The PCL segments provide the system more flexibility which helps improve its shapememory property. The decrease in flexural strength couldalso be due to the incorporation of PCLOH in the blend matrixthat decreases the effective crosslink density of epoxy-cyanateester system by matrix dilution and by plasticizingthe network.

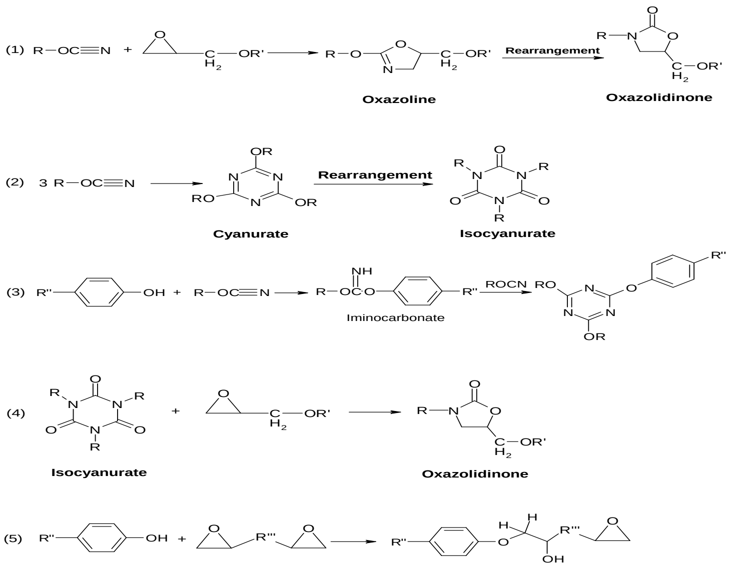

Fig 4 The reaction pathways of curing process.

Dynamic mechanical thermal properties

Visco-elastic properties of the samples were investigated by DMA in three point bending mode. **Fig 5**, indicate the loss tangent (*tanδ*) for different compositions as a function of temperature. The temperature at the maximum value of *tanδ* indicates the transition temperature (T_{trans}). A high glassy state modulus (E_g) provides the materials high shape fixity. This arises from the fact that high glassy modulus is indicative of high cohesive energy (mostly highly cross linked) which leads to minimized propensity for creep related shape change. High glassy modulus is not always mandatory for high shape fixity but is desirable, whereas the high rubbery modulus (E_r) implies high elastic recovery [4] at high temperature. The transition temperature T_{trans} is determined from the tanδ peak of the first transition. The modulus ratio E_g/E_r was taken as ($E'_{Ttrans\text{-}20}/E'_{Ttrans+20}$). Where, $E'_{Ttrans\text{-}20}$ and $E'_{Ttrans+20}$standfor the storage modulus at temperature $T_{trans\text{-}20}$ and $T_{trans+20}$, respectively. Though storage modulus decreases the Eg/Er ratio **Table 2** increases with increase in concentration of PCLOH. The latter implies a better shape memory property for PCLOH-rich system. Similarly a decreasing trend is observed in *tanδ*(transition temperature) means that PCL backbone helps increase the flexibility of the polycyanurate-oxazolidinone network. As the PCL content increases further, the system tends to be mono phasic *i.e.* PCLOH rich with a single T_{trans} drifting to the low temperature scale.

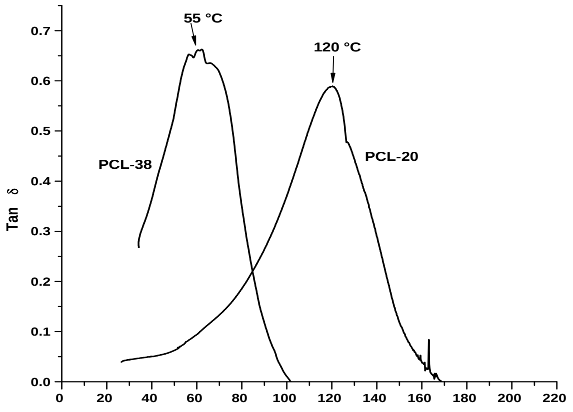

Fig 5 Loss tangent as a function of temperature of PCL-20 and PCL-38

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 behaviors of PCL-20 are demonstrated in **Fig 6**. 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, this deformed temporary shape (b) was 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 compositions were conducted in temperatures T_{trans}+20 (°C) **Table 2**. The shape recovery increases in the order PCL-20<PCL-38. This observation conforms to the trend in modulus ratio (Eg/E_r) which increases with increase in shape recovery [14]. At high E_g/E_r ratio, the shape recovery is maximum at minimal recovery time. Though the BADC rich system showed good 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 [4]. The present system possesses shape fixity to the tune 87–98% and shape recovery of 92–94 %. The advantage of this system includes controllable transition temperature and good processability than traditional shape memory thermoset system.

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	% shape recovery T_{trans}+20 (°C)	Recovery Time (min)	% shape fixity at T_{trans}-20 (°C)
PCL-20	98 ± 0.5	120	15	87	2.55	92
PCL-38	23 ± 0.5	55	20	98	1.20	94

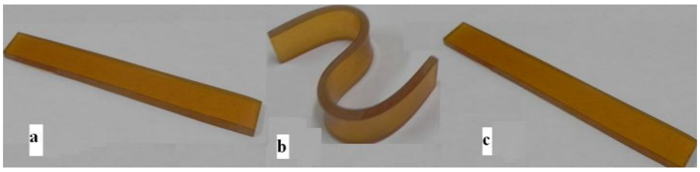

Fig 6 Shape memory properties of PCL-20 (a) original/permanent shapes, (b) fixed temporary shapes and (c) recovered shapes.

Conclusions

A shape memory thermoset polymer was designed by co-reacting cyanate ester with epoxy and a phenol-telechelicpoly(ε-caprolactone). The transition temperature of the blend decreased with increase in PCLOH content. The shape recovery increased and the recovery time decreased on increasing the shape memory polymer content in the ternary blend. The actuation temperature can be tuned by varying the PCLOH content. The polymer possessed good mechanical properties 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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