Indian Journal of Chemical Technology
Vol. 25, January 2018, pp. 68-73

# Influence of soft segments on thermo-mechanical behaviour of novel epoxy based shape memory polymers

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*Received 1 September 2016; accepted 9 February 2017*

Epoxy based Shape Memory Polymers (SMEPs) have been formulated by reacting an aerospace grade aromatic epoxy resin with aliphatic amines. TETA (triethylenetetramine) series and TTD (trioxatridecanediamine) series SMEPs with varying soft segment contents and with glass transition temperatures ($T_g$s) ranging from 103-51°C have been obtained. The viscoelastic behaviour of SMEPs has been investigated using an Advanced Rheometric Expansion System (ARES). For the thermomechanical tests, the respective $T_g$ of each SMEP has been fixed as the deformation as well as recovery temperature (shape switching temperature). Further, the effect of soft segments on thermo-mechanical shape memory behaviour of the SMEPs has been evaluated. The results reveal that TTD series SMEP with maximum soft-segment content exhibit a narrow viscoelastic region, complete shape recovery and very good shape memory behaviour. Thus based on specific applications the soft segment content may be varied suitably.

**Keywords:** Epoxy, Shape memory polymer, Soft segment, Glass transition temperature, Thermo-mechanical, $T_g$ tailoring

Shape memory polymers (SMPs) represent an important recent addition to the smart materials family[1-3]. At the molecular level, an SMP network is composed of rigid hard segments such as high molecular weight bulky aromatic groups and flexible soft segments such as low molecular weight, linear, aliphatic long chains[4,5]. Hard segments are responsible for setting the permanent shape while the soft segments enable the fixing of temporary shape and recovery of the permanent shape. In the emerging area of SMPs, extensive work has been carried out on polyurethane (PU) based SMPs[4-8] till date, since it is a low cost polymer, which can have $T_g$s nearer to room temperature and also exhibits excellent shape memory behavior. PU based SMPs are mostly used in biomedical applications due to the high elongation and low strength requirements. Influence of soft segment content on shape memory behaviour of PU based SMPs has been reported in literature[8]. Results from these studies reveal that the greater the amount of soft segment content in an SMP, lower is its $T_g$ and higher is the shape recovery rate.

Compared to PU based SMPs, lesser research content is available on epoxy based SMPs (SMEPs). Epoxy resins are widely used as structural materials in the aerospace and space applications due to their unique thermal and mechanical properties[9,10]. Hence proper characterization of the thermomechanical shape memory behavior of SMEPs assumes utmost importance. From the literature survey, it is noticed that most of the early reports on SMEPs revolved around thermomechanical tests in the tensile mode where test specimens were deformed and recovered above $T_g$[11-15]. Further the commercially available or chemically modified SMEPs were utilized for these kind of studies. Tandon *et al.*[11] studied the effects of different environments such as UV, moisture, lube oil, etc., on the thermo-mechanical behaviour of Veriflex SMEP. Xie and Rousseau[13] tailored the $T_g$ of an SMEP by changing the crosslinking density as well as incorporation of flexible groups and studied their shape memory behavior. Merlin *et al.*[14] developedSMEPs by curing DGEBA epoxy resin with amine terminated polytetramethylene oxide (PTMO) and evaluated their shape memory behaviour by bending tests using a mandrel.Apart from these studies there are a few reports on the effect of deformation temperature on the rate and extent of recovery[16-19]. But in all these studies the deformation and recovery temperatures are different. ie., if the deformation temperature is ≤ $T_g$, the recovery temperature is >$T_g$. With the final applications point of view, it is important that the deformation and recovery temperature (shape switching temperature) are one and the same. But none of these reports have studied the thermo-mechanical behaviour of SMEPs where the shape switching temperature is equal to $T_g$.

In the present work, four different SMEPs were developed by varying the soft segment content in the base aromatic epoxy resin by introducing linear aliphatic groups. The effect of soft segment content on $T_g$ and the cyclic thermo-mechanical shape memory behavior in flexure mode was studied. Further, for these studies, $T_g$ was selected as the shape switching temperature.

## Experimental Section

### Material

An aromatic epoxy resin, diglycidyl ether of Bisphenol A (DGEBA), an aliphatic epoxy resin, diglycidyl ether of butanediol(DGEBD) and an aliphatic amine hardener, triethylenetetramine (TETA) were procured from M/s. Huntsman advanced materials (India) Pvt. Ltd., Mumbai. A long chain aliphatic amine 4,7,10-trioxa-1,13-tridecanediamine (TTD)was procured from M/s. Sigma Aldrich, USA. All the chemicals were used as received.

The chemical structures of the SMEP constituents are shown in Fig. 1 and the details of compositions are given in Table 1.

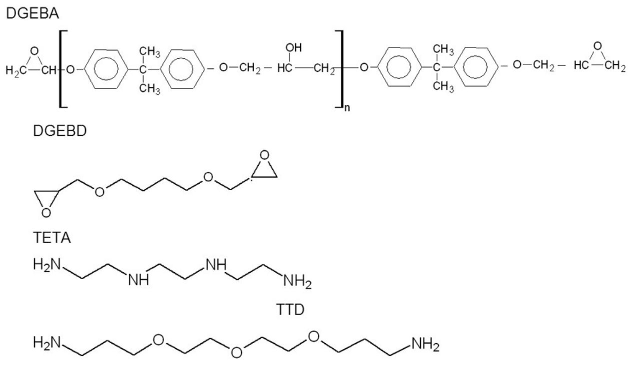

Fig. 1 — Chemical structures of the constituents of SMEPs

Table 1 — Composition details of SMEPs

| Sample code | DGEBA (g) | DGEBD (g) | TTD (g) | TETA (g) |
|---|---|---|---|---|
| TETA1 | 100 | 00 | 00 | 10 |
| TETA2 | 80 | 20 | 00 | 11 |
| TTD1 | 100 | 00 | 29 | 00 |
| TTD2 | 80 | 20 | 31 | 00 |

### Cure monitoring using FTIR spectroscopy

The curing of each formulation was monitored using an FTIR spectrometer (Vector 22 model, Bruker, Germany). Spectrum was recorded in the range of 4000-400$cm^{-1}$ and was acquired at regular intervals of time.

### Preparation of neat resin castings

Epoxy resin was heated at 80°C for 1 h and degassed under vacuum for 1 h. The resin was allowed to cool to room temperature before adding stoichiometric amounts of amine hardener (Table 1). The mixture was stirred well and degassed again for 20 min. This mixture was then poured into a metallic mould of dimensions 200 mm × 200 mm × 3 mm and cured for 24 h at room temperature. Then, the casting was released from the mould and test specimens were cut using water jet machining. A three step thermal post cure was performed for all the test specimens at 50°C - ½ h, 70°C - 1 h and 85°C - 2 h. Samples were thermally cycled between room temperature and 100°C for three times before evaluating their thermal, mechanical and shape memory behaviour, in order to remove thermal strains, if any, imposed during fabrication.

### Viscoelastic characterization

Viscoelastic behaviour was evaluated using an Advanced Rheometric Expansion System (ARES) from M/s WatersInc., USA. Rectangular test sample of dimensions 45 mm × 10 mm × 3 mm was heated from 30°C to 150°C at a heating rate of 5°C/min, 0.1% strain and 1Hz frequency using torsion rectangular geometry.

### Determination of cross-linking density

The cross-linking density ($\vartheta_e$) was calculated by the theory of rubber elasticity using the following equations[20]. The shear storage modulus in the rubbery state obtained from ARES plots was substituted in the equation to evaluate cross-linking density values for all the SMEP formulations.

$$G \cong \frac{\rho RT}{M_c} \qquad \dots (1)$$

$$\vartheta_e = \frac{\rho}{M_c} = \frac{G}{RT} \qquad \dots (2)$$

where

$G$ = Storage modulus in the rubbery state (MPa)

$M_c$ = Average molecular weight between cross-linking points (g/mol)

$\rho$ = Polymer density (g/$cm^3$)

$R$ = Universal gas constant (J/molK)

$T$ = Absolute temperature (K)

$\vartheta_e$ = Cross-linking density (mol/cm$^3$)

### Three point bending (Flexure) test

Three point bending test was carried out at room temperature to evaluate the flexural strength of the SMEPs. The test was done in accordance with ASTM D 790, using Zwick UTM (model-A150/SN5A) with a load cell capacity of 150kN. The specimen dimensions were 90 mm × 10 mm × 3 mm. The tests were conducted at a cross head speed of 2 mm/min and support span was set at 40 mm.

### Thermomechanical test

Rectangular bar specimens of dimensions 90 mm (L) × 10 mm (W) × 3 mm (t) were used to investigate the shape memory behaviour of the SMEPs.

Thermomechanical tests were carried out using the INSTRON UTM, connected with a thermal chamber. Temperature inside the chamber was measured using a K type contact thermocouple which was placed near the test sample. The test was conducted in the three point bending (flexure) mode with a crosshead speed of 2 mm/min and span length of 40 mm[21].

### Thermomechanical cycle

Prior to testing, each sample was placed on the test fixture, heated to its $T_g$ and maintained for 15 min for temperature equilibration. Typical thermomechanical cycle involves the following three steps:

1. Deformation: The heated sample was deformed to a deflection of $D_{max}$ (10 mm),
2. Cooling: Under the imposed constraint, the sample was cooled to room temperature and at this pointconstraint was removed and the deflection, $D_f$ was measured
3. Strain recovery: The sample was reheated to its $T_g$ and maintained for 15 min and the deflection $D_r$ was measured

Strains were calculated using the following equations

$$\varepsilon_{max} = \frac{6D_{max}d}{L^2} \times 100 \qquad \ldots (3)$$

$$\varepsilon_{fix} = \frac{6D_f d}{L^2} \times 100 \qquad \ldots (4)$$

$$\varepsilon_{res} = \frac{6D_r d}{L^2} \times 100 \qquad \ldots (5)$$

where

$\varepsilon_{max}$ = Maximum strain (%)

$\varepsilon_{fix}$= Fixed strain (%)

$\varepsilon_{res}$= Residual strain(%)

d= Thickness of the sample (mm)

L= Span length (mm)

The strain fixity (%) and strain recovery (%) were calculated by following equations[21]

$$\%R_f \cong \frac{\epsilon_{fix}}{\epsilon_{max}} \times 100 \qquad \ldots (6)$$

$$\%R_r \cong \frac{(\varepsilon_{max}-\varepsilon_{res})}{(\varepsilon_{max})} \times 100 \qquad \ldots (7)$$

% $R_f$ = Strain fixity (%)

% $R_r$ = Strain recovery (%)

## Results and Discussion

### Cure monitoring by FTIR spectroscopy

The epoxy-amine cure reaction was characterized by monitoring the characteristic IR absorption peak for the epoxy group (at 912 cm$^{-1}$) at regular intervals of time. From Fig. 2, it may be noticed that in case of TETA1 SMEP, the epoxy peak at 912 cm$^{-1}$ has finally disappeared, confirming completion of cure. For all the four SMEPs, completion of cure was ensured using FTIR data.

### Viscoelastic characterization

Viscoelastic behavior of SMEPs were evaluated in the torsion mode using the ARES and Fig. 3 presents the typical ARES plot obtained for TETA1 SMEP.The storage modulus (G’), loss modulus (G”) and tan δ (G”/G’) areplotted asa function of temperature from 30-150°C. The Figure also represents thegeneral characteristic of an amorphous thermoset polymer which is stiff at room temperature (glassy state) and

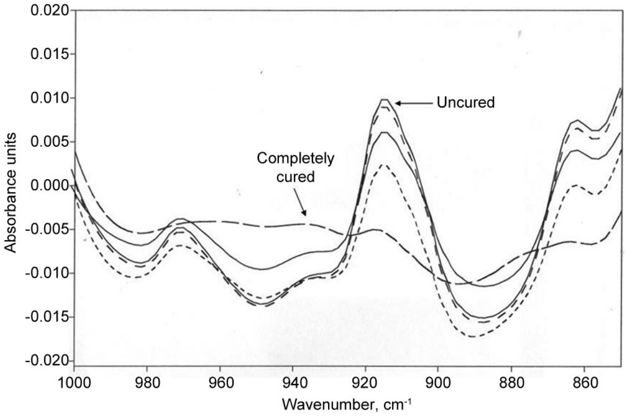

Fig. 2 — FTIR Spectra of epoxy peak of TETA1 SMEP at different time intervals of cure

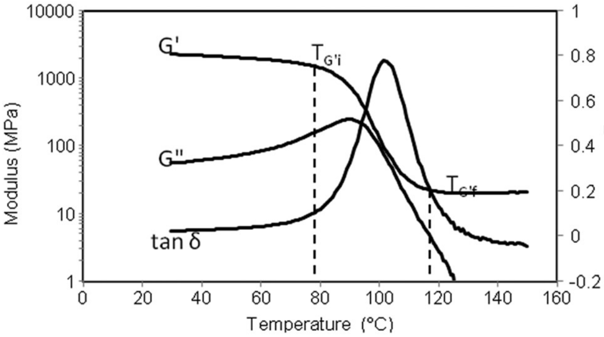

Fig. 3 — ARES plot of TETA1 SMEP

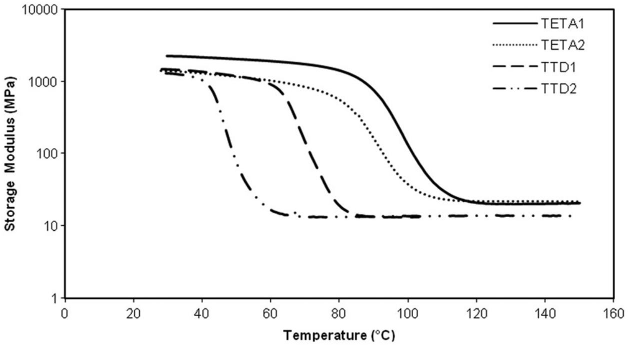

Fig. 4 — Storage modulus as a function of temperature for SMEPs

ductile at higher temperatures(rubbery state). The transition from highstiffness to low stiffness occurs at the $T_g$ (viscoelastic state). The measured peak of the tanδ curve is noted as $T_g$ of the SMEP. As is evident from the storage modulus versus temperature curve, a large change in the modulus occurs in the vicinity of $T_g$, commonly known as the viscoelastic region.

Based on the chemical reactions, percentage Soft Segments (SS) in an SMEP depends on the number of linear aliphatic groups present in it. Hence in order to correlatethe structure-property relationship, the storage modulus vs temperature curves of all the SMEPs were superimposed (Fig.4). From the figure, it is observed that,G' atglassy state(G' $_{glassy}$) is high for TETA1 compared to other SMEPs and G' at rubbery state (G'$_{rubbery}$) is low for TTD series SMEPs compared to TETA series SMEPs. TETA1 consists of least SS content and TTD2 contains maximum SS content based on corresponding chemical architecture. The flexibility of polymer chains increases with the increase in SS content and thus the $T_g$ decreases as the SS content inan SMEP increases[4,5].

As shown in Fig. 3, two temperatures, atthe start($T_{G'i}$) and end ($T_{G'f}$) of storage modulus drop were selectedin order to determine the breadth of the viscoelastic region($\Delta T_G$) presented in Table 2. From the Table, it may be noticed that the $\Delta T_{G'}$is lower forTTD series SMEPs indicating a narrow viscoelastic region and that could lead to faster shape recovery duringthermomechanical cycles.The table also reveals that both $\Delta T_{G'}$and $T_g$ are in the order of TETA1>TETA2>TTD1>TTD2.

Table 2 —Viscoelastic parameters of SMEPs

| SMEP | $\Delta T_{G'}$(°C) | . $T_g$ (°C) |
|---|---|---|
| TETA1 | 38 | 103 |
| TETA2 | 30 | 95 |
| TTD1 | 25 | 73 |
| TTD2 | 19 | 51 |

Table 3 —Crosslinking density values of SMEPs

| SMEP | G'$_{rubbery}$ (MPa) | $\vartheta_e \times 10^{-3}$ (mole/cm$^3$) |
|---|---|---|
| TETA1 | 23 | 7.08 |
| TETA2 | 23 | 7.08 |
| TTD1 | 13 | 4.37 |
| TTD2 | 13 | 4.37 |

Table 4 — Flexural test results

| SMEP | Flexural strength (MPa) | Flexural modulus (GPa) |
|---|---|---|
| TETA1 | 144 | 2.70 |
| TETA2 | 140 | 2.70 |
| TTD1 | 80 | 2.08 |
| TTD2 | 66 | 1.69 |

### Crosslinking density

For a proper understanding of shape memory behaviour, it is important to determine both viscoelastic parameters as well as the crosslinking density of the SMEPs. Hence crosslinking density was calculated from thestorage modulus in rubbery state (G'$_{rubbery}$) using equation 2 and the values are shown in Table 3. It may be noticed that the TETA series SMEPs possess higher cross-linking densities compared to TTD series of SMEPs which is in concurrence with the cure reaction.Crosslinking density plays a crucial role in quantifying the extent of strain recovery.

### Three point bending (Flexure) test results

The influence of soft segment (SS) content on mechanical properties of all the SMEPs has been quantified by carrying out 3-Point bending tests. Figure 5 shows load vs displacement curves of all SMEPs and from these data, flexural strength and modulus values were evaluated and tabulated in Table 4.

Fromflexural tests, it was observed thatTETA seriesfailed during the test at higher stress levels indicating their brittle nature whereas the degree of

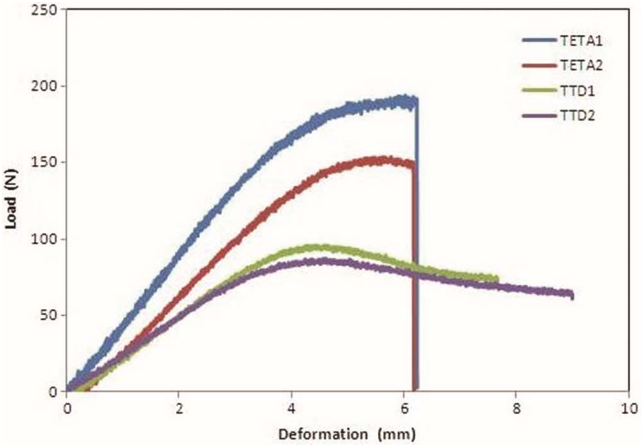

Fig. 5 — Load vs displacement curves of SMEPs

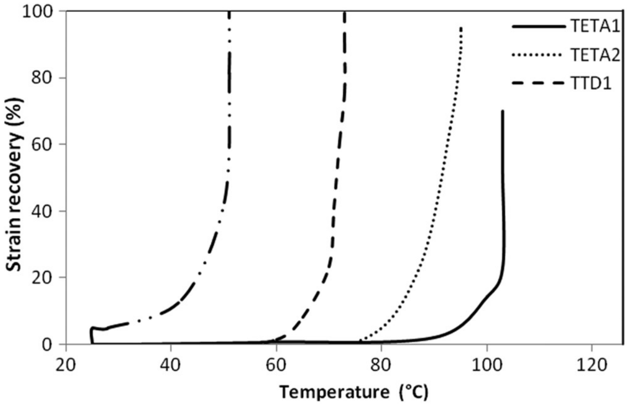

Fig. 6 — Percentage strain recovery vs temperature for SMEPs

deformation was found to be higher in TTD series with lower stress levels. TTD2 SMEP, which is considered as soft segment rich and lower crosslinking density polymer exhibited large deformation with least flexural strength and modulus values.

**Thermomechanicaltest**

The thermomechanical (TM) cycles were conducted in flexure mode by deforming and recovering the sample at their respective $T_g$s. Using equations 5 and 6, strain fixity and strain recovery of SMEPs were calculated. All the SMEPs except TTD2 showed 100% strain fixity. The strain fixity was found to be 95% for TTD2 SMEP.

For all the SMEPs, strain recovery (%) was calculated andplotted against temperature (Fig. 6). A significant strain recovery was noticed in the vicinity $T_g$. A 100% strain recovery was noticed for TTD series SMEPs where as 95% and 70% strain recovery was obtained for TETA2 and TETA1SMEPs respectively (Table 5).

Table 5 — Strain recovery results for SMEPs

| SMEP | Strain recovery (%) | Rate of strain recovery (%/min) | Soft segment content |
|---|---|---|---|
| TETA1 | 70 | 3.0 | 20.65 |
| TETA2 | 95 | 18.0 | 41.22 |
| TTD1 | 100 | 17.0 | 33.26 |
| TTD2 | 100 | 64.0 | 50.46 |

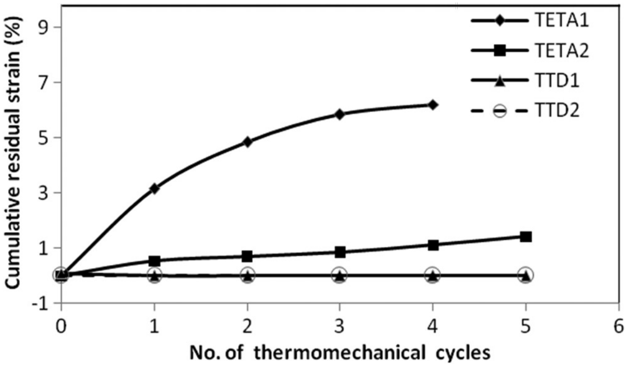

Fig. 7 — Residual strain as a function of number of shape memory cycles for SMEPs

These results clearly indicate that shape memory property depends mainly on the chemical structure of the polymer. When the crosslinking density decreases, the flexibility in the polymer increases and it leads to lowering of $T_g$ and narrowing of the viscoelastic region. The shape recovery rate increases with the increase in flexibility. In the case of TETA1 SMEP, the rigid and heavy aromatic groups present in the polymer chain obstruct and hinder complete recovery of the original shape.

Further, cyclic behaviour was assessed by calculating residual strains after each TM cycle. Except TETA1, all SMEPs were tested for 5 TM cycles due to the significantly large residual strains observed in case of TETA1 SMEP. In general residual strains are the irrecoverable strains that remain in an SMEP after being subjected to a complete TM cycle. Residual strains were plotted against number of cycles (Figure 7). For TTD series SMEPs, 0% residual strain was obtained for all TM cycles indicating complete recovery in all cycles, whereas cumulative residual strain increased with successive TM cycles for TETA series SMEPs.

## Conclusion

TETA and TTD series SMEPs with $T_g$ ranging from 103 to 51°C have been formulated by chemical incorporation of linear chains (acting as soft segments) into the base epoxy resin. Thermomechanical tests are carried out by selecting their respective $T_g$s as the shape switching temperature. Based on thermomechanical tests, it is observed that TTD series SMEPs exhibit excellent shape memory behavior when deformed and recovered at $T_g$. Due to the presence of higher soft segment content andnarrow viscoelastic region and lower crosslinking densities 100% strain recovery coupled with fastest rate of recovery was obtained for TTD2 SMEP.

With regard to TETASMEPs, 100% strain recovery could not be achieved . TETA1 exhibit lowest rate and extent of strain recoverywhich is attributed to the significantly broad viscoelastic region ($\Delta$ $T_G$). These results confirm that the rate and extent of strain recovery is a combined effect of the soft segment content and crosslinking density of SMEP formulations. The present work highlights the fact that for specific application requirements, desired $T_g$, rate and extent of strain recovery, the SMEP could besuitable tailoredby appropriately changing the chemistry.

## Acknowledgement

Authors wish to acknowledge the financial assistance rendered by NPMASS, ADA. Further they wish to thank their colleagues Dr. A. Vanaja, Mr. Chiranjeevi M.C and Mr. H.V. Ramachandra for their support during the experimental work.

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