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Estimation of Creep and Recovery of Carboxyl-terminated Butadiene Acrylonitrile-epoxy Shape Memory Polymers under Tensile Loading

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ABSTRACT
The creep and recovery of 5% carboxyl-terminated butadiene acrylonitrile (CTBN) modified epoxy shape memory polymers (SMP) was studied. The results were compared with those for the unmodified epoxy SMP. The glass transition temperatures (T_g) were determined using Advanced Rheometric Expansion System (ARES). The creep behavior of the unmodified epoxy and 5wt.% CTBN modified epoxy SMP were studied through short-term tensile creep test. These tests were carried out at different temperatures ranging from glassy, viscoelastic, and rubbery regimes and different loading conditions. It was observed that T_g is slightly reduced by the addition of CTBN in the SMP. For both the SMPs, the creep strain increases with increasing temperature and shows a maximum in the vicinity of the T_g. Furthermore, creep strain increases with increasing load in the glassy and rubbery regimes. A mutual comparison revealed that the creep strain was higher for unmodified epoxy SMP than that of 5% CTBN modified epoxy SMP at all the temperatures considered. A higher percentage creep recovery was noticed in the case of the CTBN modified epoxy SMP as compared to the unmodified epoxy SMP.

Key words: *Creep deformation, Recovery, Carboxyl-terminated butadiene acrylonitrile, Epoxy, Shape memory polymers, Tensile.*

1. INTRODUCTION

Shape memory polymers (SMPs) are those materials that have the ability to “memorize” a permanent shape when “fixed” to a temporary shape under specific conditions of temperature and stress [1-7]. SMPs have aroused great attention from scientists and engineers due to their capacity to remember two shapes at different conditions. This gives these materials great potential for application as sensors, actuators, smart devices, and media recorders.

In a real life scenario, during usage, polymeric materials are frequently subjected to different stresses over a period. The materials are commonly placed under a load for a long duration, or the stress is repeatedly applied in a working environment. Therefore, the mechanical response, notably the instantaneous and time-dependent deformation is significant for material applications, which require dimensional stability. Creep test is an essential method to obtain information about the material deformation [8-10]. The creep deformation is a big barrier for polymers to satisfy the requirements in long-term loading service because the accumulated strain might exceed the material’s deformation limitation and lead to the creep fracture of the structure. Hence, it is of great importance to know about the creep properties of SMPs.

Creep is one of the viscoelastic parameters of SMPs which depends heavily on the material temperature. During a typical shape memory cycle, the polymer experiences different temperature regimes. Hence, it is very essential to study the creep behavior at different temperatures ranging from glassy to rubbery regimes of SMPs. Plaseied and Fatemi [11] studied the tensile creep behavior of vinyl ester polymer and functionalized carbon nanofiber-based nanocomposite. The results suggested that, at lower temperatures, higher creep compliance was observed for vinyl ester as compared to nanocomposite, while at temperatures close to T_g of vinyl ester creep compliance in nanocomposite was higher than that for vinyl ester. Liang and Song [12] have studied the shape memory effect and creep behavior of an epoxy SMP filled with carbon black. The results show that the SMPs exhibit excellent shape memory behavior together with significantly improved creep resistance. Creep behavior of polyurethane-based SMP was

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investigated by Struik [13]. He considered the effect of physical aging on the creep behavior. Zhang *et al*. [14] studied the viscoelastic creep of vertically aligned carbon nanotubes using nanoindentation method. Characterization of viscoelastic behavior of epoxy SMPs was carried out by Song and Wang [15]. They studied the stress-strain hysteresis, stress relaxation, and creep behavior at different temperatures. Ohki *et al*. [16] studied the creep and cyclic mechanical properties of SMPs. Their studies confirmed that fiber reinforcement could be used to improve creep properties.

In this study, the creep and recovery profile of unmodified and 5% carboxyl-terminated butadiene acrylonitrile (CTBN) modified epoxy SMP has been investigated as a function of different temperatures as well as loading conditions.

2. EXPERIMENTAL

2.1. Materials and Specimen Preparation

A thermosetting epoxy-based SMP was obtained by co-reacting L552 epoxy resin (epoxy equivalent weight [EEW] of 156 g/eq) with K552, a cycloaliphatic amine hardener, supplied by M/s. Atul India (P) Ltd., Mumbai, India. This SMP was modified with 40 wt.% CTBN-epoxy adduct (Albipox 1000, EEW = 330 g/eq), procured from Nanoresins, Geesthacht, Germany so as to yield 5% CTBN (by weight) - modified epoxy SMP matrices. The unmodified and CTBN modified SMPs were prepared as per the procedure mentioned elsewhere [17]. Before subjecting to tests, the specimens were thermally cycled between 25°C and 100°C so as to remove the thermal strains accumulated during fabrication.

2.2. Glass Transition Temperature (T_g)

An Advanced Rheometric Expansion System (ARES, Waters Inc., USA) was used to measure the glass transition temperature of the 0 and 5% CTBN modified SMPs in the temperature range of 25-150°C (heating rate: 5°C/min) at a strain of 0.1% and a frequency of 1 Hz. The samples with dimensions of 45 mm × 10 mm × 2 mm were tested using a torsion rectangular geometry.

2.3. Creep Tests

From the ARES plots of unmodified and CTBN modified epoxy SMPs, specific temperatures ranging from glassy to rubbery regimes were selected. The creep and recovery tests were performed using a custom-built thermo-mechanical creep facility with microprocessor based temperature controller to control the temperature (M/s Spranktronics Pvt Ltd., Bengaluru). Test specimens with dimensions of 90 mm × 10 mm × 3 mm were used for the creep tests. The specimens were mounted carefully in a fixture and aligned to avoid any twisting or buckling of the specimens. The distance between the tension grips was maintained at 40 mm, and this was considered as the gauge length. Initially, the specimen was kept for 10 min at the corresponding test temperature to attain the thermal equilibrium and then preselected constant load (in the elastic region of stress-strain curve) was applied onto the specimen for about 3600 s. Then, the load was removed immediately and creep recovery was measured over a recovery time of 3600 s. The increase in gauge length was measured using displacement sensor (LVDT) for strain calculations. After 3600 s, the unrecovered strain was measured, and recovery ratio (R_r) was calculated as per the Equation (1) [18].

$$R_r(\%) = \frac{\varepsilon(t_0) - \varepsilon(t_0, t)}{\varepsilon(t_0)} \times 100 \quad (1)$$

Where, $\varepsilon(t_0)$ is the maximum creep strain and $\varepsilon(t_0,t)$ is the unrecovered strain.

After completion of the test, the lower grip was released, and the specimen was kept for 10 min at the corresponding temperature. The grips were applied again and creep test was continued for the next pre-selected stress level. Creep tests were performed at different stress levels and temperatures (25°C, 80°C, 103°C, and 120°C).

3. RESULTS AND DISCUSSIONS

3.1. T_g Determination by ARES

ARES plots of storage modulus (G’), loss modulus (G”), and tan δ versus temperature for epoxy SMP and 5% CTBN-epoxy SMP are shown in Figure 1a and b, respectively. The tan δ peaks indicate the T_g values of 103°C and 100°C for epoxy SMP and 5% CTBN-epoxy SMP, respectively. From the Figure 1, it was observed that T_g was slightly reduced by the addition of CTBN.

Different temperatures were selected from ARES plots for examining the creep response and are presented in Figure 1a and b and Table 1.

3.2. Creep and Recovery behavior of SMPs

3.2.1. Influence of temperature

The creep and recovery of epoxy SMP and 5% CTBN-epoxy SMP were investigated under different temperatures. The creep strain and residual strains as a function of time for epoxy SMP and 5% CTBN-epoxy SMP are presented in the Figures 2a-d and 3a-d, respectively. The creep strain increases with increasing temperature and peaks at around the T_g in both the SMPs. When the SMP is at $T < T_g$ (i.e., 25°C), the mobility of the molecular chains is restricted, so the creep strain is small. Furthermore, the polymer molecules are frozen, and so they can suffer a relatively high stress and thus induce a small permanent strain.

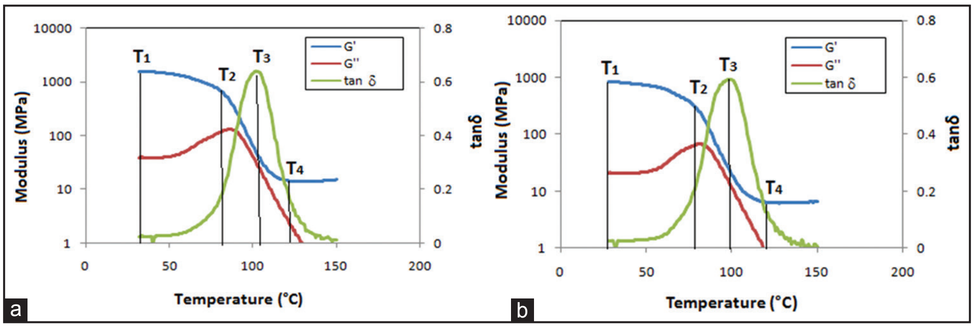

Figure 1: Advanced Rheometric Expansion System plots of: (a) Epoxy shape memory polymers (SMP) and (b) 5% carboxyl-terminated butadiene acrylonitrile-epoxy SMP.

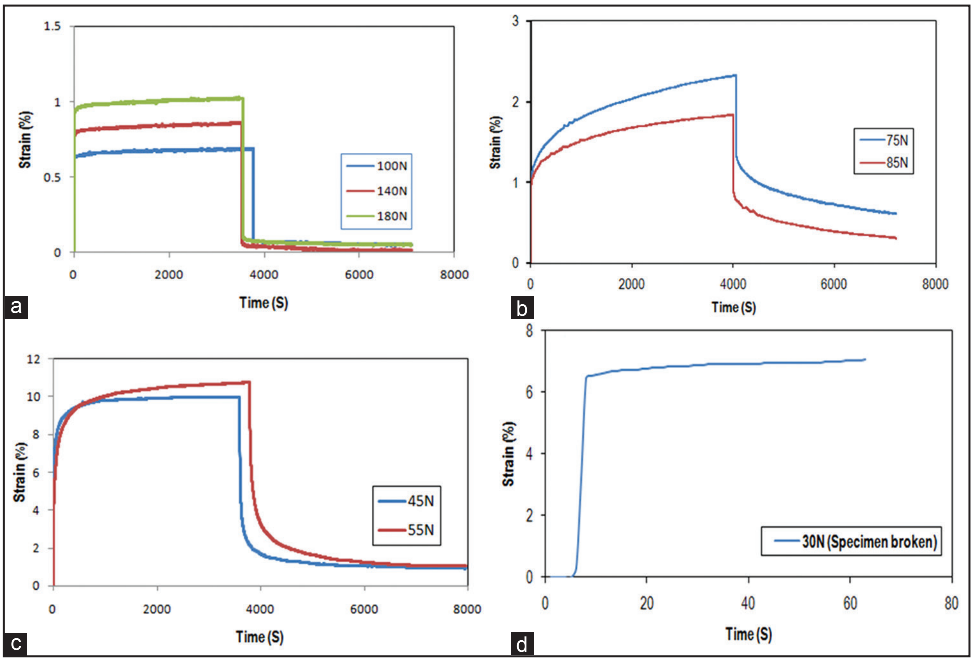

Figure 2: Creep and recovery of epoxy shape memory polymers at different temperatures: (a) 25, (b) 80, (c) 103, and (d) 120°C.

However, at a relatively high temperature near the glass transition region (i.e., 80°C and 103°C), the SMP becomes flexible and is easy to deform due to the high mobility and large relaxation of polymer chains. Furthermore, the molecular motion and rearrangement can occur drastically at this region, thus leading to considerable permanent deformation. However, at $T > T_g$ (i.e., 120°C), the SMPs tend to exhibit rubber elasticity, become more flexible and recover easily. Therefore, the recovery ratio is maximum in the rubbery regime.

3.2.2. Influence of applied load

It can be seen from the Figures 2a-d and 3a-d that the SMPs showed different responses to applied load levels. The creep strain increased with the increasing load at 25°C, 103°C, and 120°C in case of 5% CTBN-epoxy SMP. However, the unmodified epoxy SMP could not withstand the load at 120°C and failed during load application itself. Specifically for the creep tests at 80°C, the creep strain decreased slightly with increasing load in both the SMPs. This may be due to the accumulation of unrecovered strain after the first applied load. Further, it was found that higher loads resulted in higher recovery ratio (calculated using Equation 1) as listed in Tables 2 and 3 for both SMPs.

Table 1: Temperatures selected for creep tests.

Codes	Temperatures (°C)	Regimes
T_1	25	Glassy
T_2	80	Viscoelastic
T_3	103	Glass transition
T_4	120	Rubbery

3.3.3. Influence of CTBN

From the Figure 3a-d and Table 3, it can be seen that the creep strain of 5% CTBN-epoxy SMP is lower

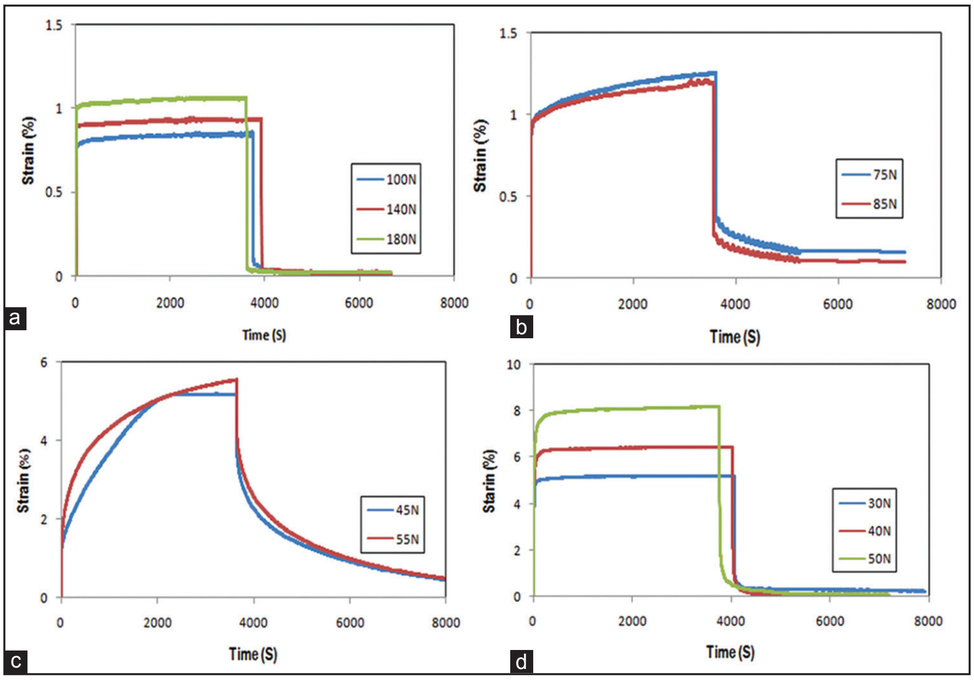

Figure 3: Creep and recovery of 5% carboxyl-terminated butadiene acrylonitrile-epoxy shape memory polymers at different temperatures: (a) 25°C, (b) 80°C, (c) 103°C, and (d) 120°C.

Table 2: Creep and recovery properties of epoxy SMP under different temperatures and loads.

Temperature (°C)	Load (N)	Creep strain (%)	Residual strain (%)	Recovery ratio (%)
25	100	0.71	0.02	97.18
	140	0.89	0.01	98.87
	180	1.19	0.02	98.31
80	75	2.33	0.62	73.51
	85	1.84	0.29	83.85
103	45	9.98	0.92	90.78
	55	10.75	0.86	92.00
120	30	7.83 (specimen broken)		

SMP=Shape memory polymers

Table 3: Creep and recovery properties of 5% CTBN-epoxy SMP under different temperatures and loads.

Temperature (°C)	Loads (N)	Creep strain (%)	Residual strain (%)	Recovery ratio (%)
25	100	0.84	0.01	98.22
	140	0.93	0.01	98.92
	180	1.06	0.02	98.11
80	75	1.25	0.09	92.40
	85	1.19	0.07	94.53
103	45	5.54	0.45	91.87
	55	5.72	0.53	90.73
120	30	5.20	0.13	97.50
	40	6.44	0.02	99.68
	50	8.16	0.08	99.01

CTBN=Carboxyl-terminated butadiene acrylonitrile, SMP=Shape memory polymers

than that of the epoxy SMP under all the temperatures and loads considered. This implies that the creep behavior has improved due to the presence of CTBN phase [19] in the epoxy SMP. Furthermore, the 5% CTBN-epoxy SMP shows lower residual strains than the epoxy SMP indicating that incorporation of CTBN decreases the permanent deformation remarkably, and the recovery ratio is increased particularly in high-temperature regimes. At 120°C, the 5% CTBN-epoxy SMP could withstand all the three loads due to the flexibility and toughening effect of the rubber particles dispersed in the epoxy SMP. Furthermore, maximum recovery was noticed in this region. CTBN modification thus results in higher creep recovery in all the temperature and loading conditions. These findings also suggest that creep and recovery behavior are suitable indicators for the impact of the filler loading [20].

4. CONCLUSIONS

The creep and recovery behavior of a CTBN-epoxy SMP at different temperatures and loads has been compared with that of the corresponding epoxy SMP. The following conclusions were drawn:

The creep strain increases with increasing temperature and shows maximum around the T_g in both the SMPs.

The creep strain increased with the increasing load at 25°C, 103°C, and 120°C, however, at 80°C, the creep strain decreased slightly with increasing load in both the SMPs. This may be due to the accumulation of unrecovered strain after the first applied load. Incorporation of CTBN into epoxy SMP produced a significant decrease in the residual strain. In the rubbery regime, the CTBN-epoxy SMP withstood the applied loads in contrast to the unmodified epoxy SMP, which failed during load application itself. A higher percentage creep recovery was noticed in the case of the CTBN-epoxy SMP as compared to the epoxy SMP, thus confirming the improved creep resistance of the former.

5. REFERENCES

1. C. Liu, S. B. Chun, P. T. Mather, L. Zheng, E. H. Haley, E. B. Coughlin, (2002) Chemically cross-linked polycyclooctene: Synthesis, characterization, and shape memory behavior, ***Macromolecules***, **35(27):** 9868-9874.
2. K. Nakayama, (1991) Properties and application of shape-memory polymers, ***International Journal Polymer Science and Technology***, **18:** T43-T48.
3. G. J. Monkman, (2000) Advances in shape memory polymer actuation, ***Mechatronics***, **10:** 489-498.
4. J. Morshedian, H. A. Khonakdar, S. Rasouli, (2005) Modeling of shape memory induction and recovery in Heat shrinkable polymers, ***Macromolecular Theory and Simulations***, **14:** 428-434.
5. K. Otsuka, C. M. Wayman, (1998) ***Shape Memory Materials***, New York: Cambridge University Press.
6. A. S. Lendlein, S. Kelch, (2002) Shape-memory polymers, ***Angewandte Chemie***, **41:** 2034-2057.
7. A. S. Lendlein, S. Kelch, K. Kratz, J. Schulte, (2005) Shape-memory polymers. In: ***Encyclopedia of Materials***, Amsterdam: Elsevier, p1-9.
8. M. Tehrani, M. Safdari, M. S. Al-Haik, (2011) Nano characterization of creep behavior of multiwall carbon nanotubes/epoxy nanocomposite, ***International Journal of Plasticity***, **27(6):** 887-901.
9. M. Gan, B. K. Satapathy, M. Thunga, R. Weidisch, P. Potschke, A. Janke, (2007) Temperature dependence of creep behavior of PP-MWNT nano composites, ***Macromolecular Rapid Communications***, **28(16):** 1624-1633.
10. R. H. Varela, M. Weisenberger, D. R. Bortz, G. I. Martin, (2010) Fracture toughness and creep performance of PMMA composites containing micro and nanosized carbon filaments, ***Composites Science and Technology***, **70(7):** 1189-1195.
11. A. Plaseied, A. Fatemi, (2009) Tensile creep and deformation modeling of vinyl ester polymer and its nanocomposite, ***Journal of Reinforced Plastics and Composites***, **28(14):** 1775-1788.
12. X. Y. Liang, J. Y. Song, (2013) Shape memory effect and viscoelastic behavior of SMP epoxy filled with carbon particles, ***High Performance Polymer***, **25:** 254-259.
13. L. C. E. Struik, (1978) ***Physical Aging in Amorphous and Other Materials***, New York: Elsevier.
14. Q. Zhang, Y. C. Lu, F. Du, L. Dai, J. Baur, D. C. Foster, (2010) Viscoelastic creep of vertically aligned carbon nanotubes, ***Journal of Physics D: Applied Physics***, **43:** 1-7.
15. W. B. Song, Z. D. Wang, (2013) Characterization of viscoelastic behaviour of shape memory epoxy systems, ***Journal of Applied Polymer Science***, **128:** 199-205.
16. T. Ohki, Q. Q. Ni, M. Iwamoto, (2011) Creep and cyclic mechanical properties of composites based on shape memory polymer, ***Science and Engineering of Composite Materials***, **11(2-3):** 137-148.
17. R. Kavitha, A. Revathi, S. Rao, S. Srihari, G. N. Dayananda, (2012) Characterization of shape memory behaviour of CTBN-epoxy resin system, ***Journal of Polymer Research***, **19:** 9894.
18. Y. Jia, Z. Jiang, J. Peng, X. L. Gong, Z. Zhang, (2012) Resistance to time-dependent deformation of polystyrene/carbon nanotube composites under cyclic tension, ***Composites: Part A***, **43:** 1561-1568.
19. P. Brahmananda, P. Raju, (2011) Viscoelastic response of graphite platelet and CTBN reinforced vinyl ester nano composites, ***Materials Sciences and Applications***, **2:** 1667-1674.
20. X. Wang, L. X. Gong, L. C. Tang, K. Peng, Y. B. Pei, L. Zhao, L. B. Wua, J. X. Jiang, (2015) Temperature dependence of creep and recovery behaviours of polymer composites filled with chemically reduced graphene oxide, ***Composites: Part A***, **69:** 288-298.

***Bibliographical Sketch**

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