

Estimation of creep and recovery behavior of a shape memory polymer

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Abstract The shape recovery and shape fixity properties of shape memory polymers (SMPs), advanced functional materials, were investigated in this study. Although the shape recovery behavior of these polymers has been examined from a viscoelastic point of view, questions remain with regard to quantifying the recovery behavior of SMPs. SMPs can recover their shape after the molding process; this recovery occurs via creep recovery and/or shape recovery; an estimation of SMP recovery requires a good understanding of both processes. In this study, the time–temperature superposition principle was applied to the creep and shape recovery behavior of SMPs. The creep behavior was estimated using an experimentally obtained master curve and time–temperature shift factors. Our estimated results were in good agreement with the experimental data. However, the estimation of the creep recovery with changing temperature below or above the glass transition temperature was not successful due to the lack of consideration of the shape recovery behavior. The time and temperature dependency of the shape recovery were confirmed for creep behavior, using the master curve for the recovery ratio and the corresponding shift factors for shape recovery. The values of the shape recovery shift factors differed from those for the time–temperature shift factors obtained for creep behavior. Therefore, these shape recovery shift factors were used in the estimation of creep and shape recovery behavior using the master curve for the creep tests. The estimated results were closer to the results obtained experimentally. Moreover, our results indicated that the recovery behavior above T_g was dominated by shape recovery as a result of polymer viscoelasticity.

Keywords Creep · Shape memory polymer · Shape recovery · Time–temperature superposition principle · Viscoelasticity

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1 Introduction

Shape-memory polymers (SMPs) are functional materials that respond to a specific temperature event by generating a shape change (Nakayama 1991; Otsuka and Wayman 1998; Monkman 2000; Lendlein and Kelch 2002; Lendlein et al. 2005). Such polymers have the viscoelastic characteristics of a macromolecule, along with mechanical characteristics that change dramatically with time and temperature.

Creep behavior is one of the viscoelastic behaviors of SMPs. This remarkable phenomenon is observed at temperatures above or below the glass transition temperature, T_g . SMPs also undergo shape recovery as a result of viscoelastic behavior of the polymers.

Nguyen (Nguyen et al. 2008) reviewed recent advances in constitutive modeling of thermally induced and photo-induced shape-memory behavior in polymers. This review highlights prominent constitutive models for the glass transition mechanism of amorphous networks as well as models for the crystallization and melt transition of semicrystalline materials and photo-induced network rearrangements of light-activated shape-memory polymers, and discusses future directions for modeling the shape-memory behavior of polymers. In the recent literature, modeling of the SMP behavior (Tobushi et al. 1997; Diani et al. 2006, 2012; Heuchel et al. 2010; Hong et al. 2007; Lin and Chen 1999; Morshedian et al. 2005; Nguyen et al. 2008, 2013; Srivastava et al. 2010; Xu and Li 2010; Liu et al. 2006; Kafka 2008; Muller and Pretsch 2010; Arrieta et al. 2014a, 2014b; Azra et al. 2011), especially polyurethane based polymer's modeling (Liu et al. 2006; Kafka 2008; Muller and Pretsch 2010), can be categorized into two main approaches: (i) purely elastic models that describe an amorphous cross-linked SMP as a two-phase material composed of a glassy phase and a rubbery phase, and (ii) thermo-mechanical models that describe the SMPs in terms of their viscoelastic properties. With the elastic model, the stiffness of each phase is required to predict the stiffness of the two-phase composite material. The thermo-mechanical model for SMPs has been adopted by many researchers. Intermediate models that combine the two methods described above have been used to define two-phase viscoelastic mixtures (Diani et al. 2006, 2012; Liu et al. 2006; Kafka 2008; Arrieta et al. 2014a). In general, numerous studies have attempted to simulate and predict the shape memory behavior of materials.

Typically, the shape recovery behavior was investigated in simple models such as uniaxial or torsion experiments and constitutive models (Tobushi et al. 1997; Diani et al. 2006, 2012; Heuchel et al. 2010; Hong et al. 2007; Lin and Chen 1999; Morshedian et al. 2005; Nguyen et al. 2008, 2013; Srivastava et al. 2010; Xu and Li 2010; Liu et al. 2006; Kafka 2008; Muller and Pretsch 2010; Arrieta et al. 2014a, 2014b; Azra et al. 2011); however, complex stress conditions such as in a bending model were adopted in few papers. In a previous study (Struik 1978), creep behavior of polyurethane based SMP was investigated, and the prediction of the creep behavior considering the effect of physical aging was carried out. In this study, to better understand creep and shape recovery behavior, creep tests and shape recovery tests in a bending mode were carried out on SMPs at elevated temperatures. The results from experimental tests were used to create a master curve describing the time-temperature relationship associated with not only creep but also recovery behavior of SMPs, and the prediction of the creep and shape recovery behavior was carried out considering the two-phase linear viscoelastic theory.

Fig. 1 Shape memory and shape recovery cycle of shape memory polymer

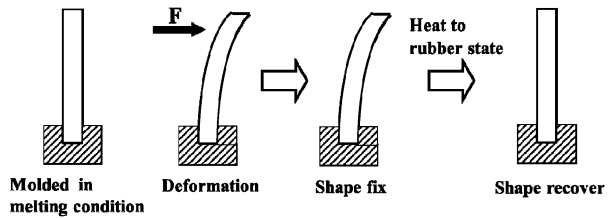
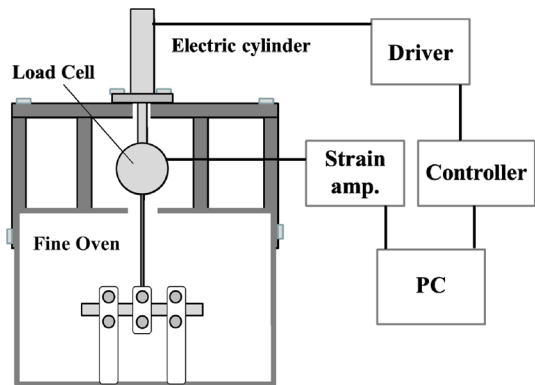


Fig. 2 Schematic drawing of load-controlled testing machine



2 Materials and experimental procedure

Polyurethane SMP (DiARY MM-9020, Mitsubishi Heavy Industries, Tokyo, Japan) was used in this study. The specimens were injection molded to create a rectangular shape (width, 10 mm; length, 70 mm; height, 3 mm).

Struik recommended producing master curves solely from momentary creep data, i.e., from creep test data, such that $t_t \leq t_a/10$, where t_t is the test time and t_a is the length of the aging treatment (Sakai et al. 2007). Based on this recommendation, the creep test performed after heat treatment for $t_a(10(t_t))$ is referred to as the short-term method. Using this method, the results from the creep test differ slightly according to the effects of physical aging.

Figure 1 shows the shape memory and shape recovery cycle of an SMP. Creep tests were carried out using the three-point bending test method. The tests were performed using the creep-testing machine shown in Fig. 2, equipped with a fine oven (Yamato Fine Oven DH42; Yamato, Tokyo, Japan). The temperature during testing ranged from 50 to 120 °C in an air atmosphere. The creep testing machine was a displacement control type; the load was controlled by a feedback circuit. The chuck parts of the three-point bending test apparatus consisted of supports and pins for load application; the pins could be rotated smoothly. The applied load for the creep tests was 10 % of the bending strength (8 MPa for the polyurethane SMPs), and the load was applied for 5 seconds. The span length was 50 mm.

The thermal properties of the SMP were investigated in a previous study by using Differential Scanning Calorimetry (DSC) (Struik 1978). Figure 3 shows the result of DSC measurement. The material of 10 mg was heated from room temperature to 200 °C with the heating rate 10 °C/min in air atmosphere. In this result, the glass transition temperature, T_g , of the SMP is 87 °C. No endothermic peaks following crystallization were observed on the DSC curve (Fig. 3). The water absorption for the SMP material was minimal.

Fig. 3 Thermal properties of the shape memory polymer obtained using differential scanning calorimetry

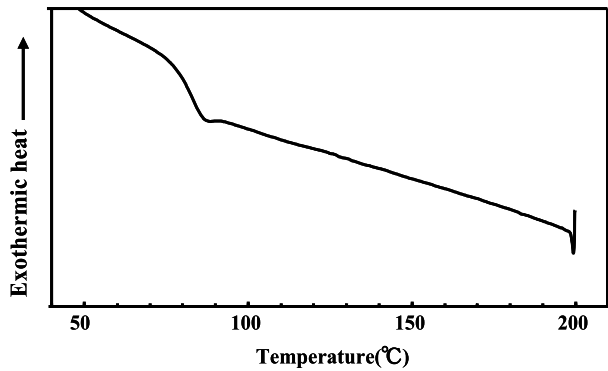
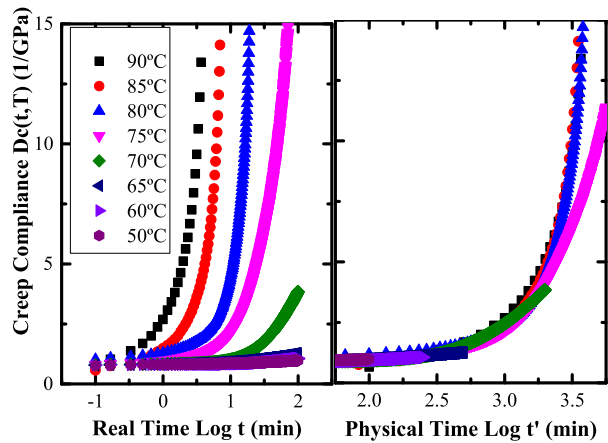


Fig. 4 Creep compliance curves and the corresponding master curve of the SMP. The reference temperature was 50 °C



3 Time–temperature dependency of the creep behavior

Three-point bending creep tests were performed on the SMP specimens, using the short-term method and various elevated temperatures. The creep deformation was evaluated according to viscoelastic theory, using the creep compliance function $D_C(t)$. This value is based on the linear viscoelastic equation for creep strain as follows:

$$\epsilon(t) = \int_{-\infty}^t D_C(t - \tau, T) \frac{d\sigma}{d\tau} d\tau. \quad (1)$$

To clarify the creep phenomena, creep compliance curves were drawn for each test temperature, as shown in Fig. 4(a). Higher temperatures during testing and longer creep test times resulted in higher creep compliance. The time–temperature superposition principle is described by the master curve of creep compliance, shown in Fig. 4(b), for a reference temperature of 50 °C. To produce the master creep compliance curve, the creep compliance curves were shifted horizontally until they overlapped the curve for the reference temperature completely. The master curve was obtained by replacing the real time t for each shifted curve by the physical time t' at the reference temperature T_0 . The time–temperature shift factor is defined as the amount of shift required to create the master curve.

The shift factor curve for the SMP is plotted as an Arrhenius-type plot (Fig. 5); this curve is a straight line at temperatures above 50 °C, demonstrating that the creep phenomenon

Fig. 5 The time–temperature shift factor of the SMP. The reference temperature was 50 °C

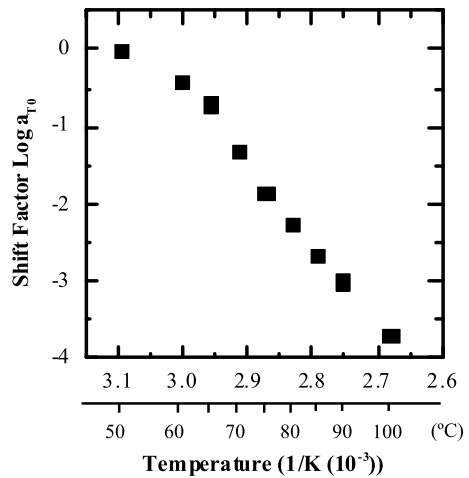
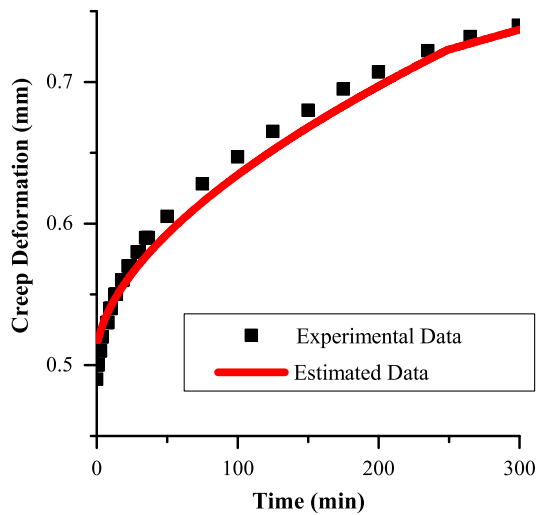


Fig. 6 Comparison between the estimated and experimental creep data. The temperature was 45 °C, the creep time was 300 min, and applied stress was 10 MPa



complies with the time–temperature superposition principle. The mechanical response at elevated temperatures confirmed the linear relationship.

4 Estimation results for creep behavior

An estimation of creep deformation was carried out using the reverse procedure of creating a master curve (Sakai and Somiya 2011). Creep deformation under arbitrary conditions can be estimated using only the master curve and time–temperature shift factors. In a previous study, the effect of physical aging was considered to estimate long-term creep behavior (Kafka 2008). In this study, it is not necessary to consider this effect because the creep tests were carried out with the short-term method.

The experimental data and estimated values are compared in Fig. 6. The test conditions were as follows: temperature, 45 °C; creep time, 300 min; and applied stress, 10 MPa.

Fig. 7 Comparison of the experimental creep and creep recovery data with the estimated data. The temperatures were 50 °C and 65 °C, the creep time was 100 min, the creep recovery time was 100 min and the applied stress was 10 MPa

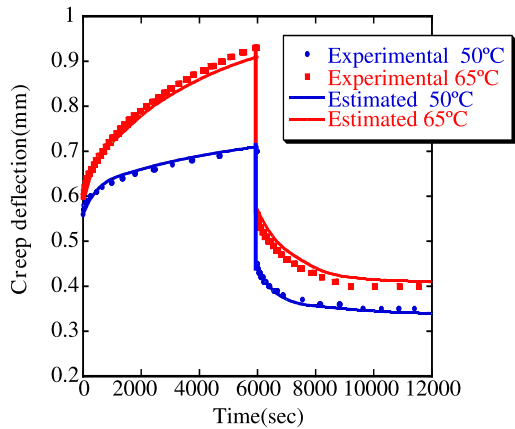
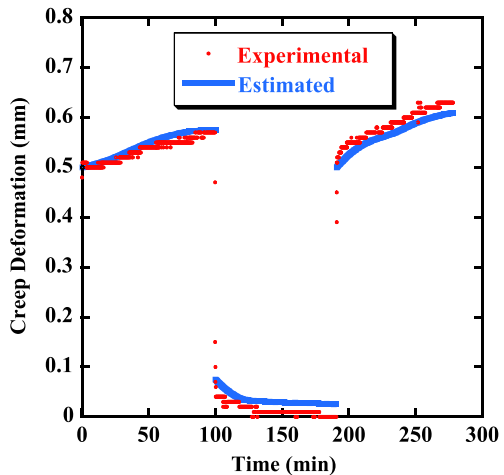


Fig. 8 Comparison between the experimental and estimated creep and creep recovery. The temperature was 55 °C and the applied stresses were 10, 0, and 10 MPa



Based on this test, the creep deformation was calculated from the master curve and time–temperature shift factor; the estimated values were in good agreement with the experimental data. Figures 7, 8, 9 show the results of the creep test estimations with changes in the applied load.

Figure 10 shows the estimation results for changes in temperature above and below T_g ; below T_g , there was good agreement between the estimated and experimental values. However, in the transition temperature region, the estimated and experimental values differed considerably. The experimental data revealed not only creep recovery behavior but also shape recovery behavior of SMP. Therefore, it is a vitrification/devitrification mechanism, which guides the shape recovery behavior of SMP.

5 Time–temperature dependency on shape recovery behavior

This section discusses the shape recovery behavior. Shape recovery tests were carried out using the same testing apparatus as used for the creep tests.

Fig. 9 Comparison between the experimental and estimated creep and creep recovery. The temperature was 45 °C and the applied stresses were 10, 20, and 0 MPa

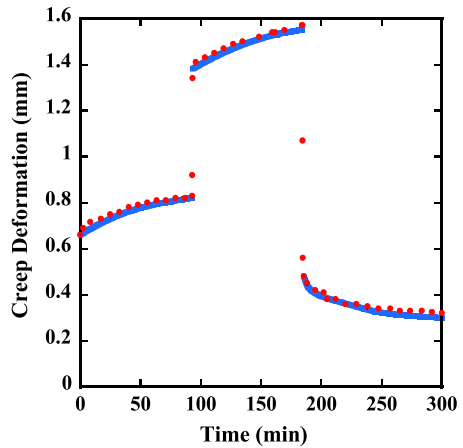


Fig. 10 Estimated results of the changes in temperature above and below T_g

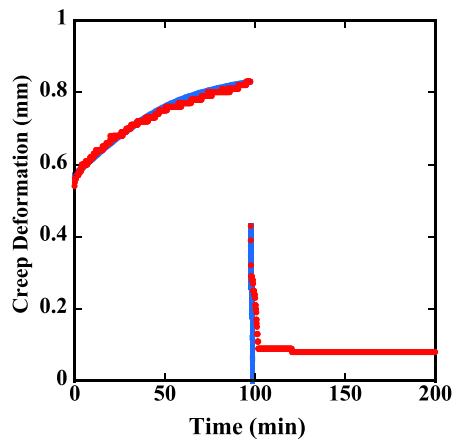
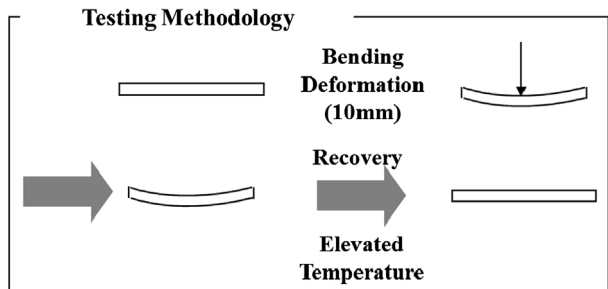


Fig. 11 Schematic diagram showing the shape recovery testing methodology



The testing methodology is shown in Fig. 11. The samples were first bent by ~10 mm and then placed in the creep testing machine. The creep testing machine controlled the jigs for application of stress under negative deformation. The deformation, application time, and temperature were recorded by a personal computer.

Figure 13 shows the results of the shape recovery tests. The shape recovery ratio was plotted on the vertical axis. When the shape recovery ratio was 100 %, the material fully

Fig. 12 The shape recovery ratio plotted on a linear time scale

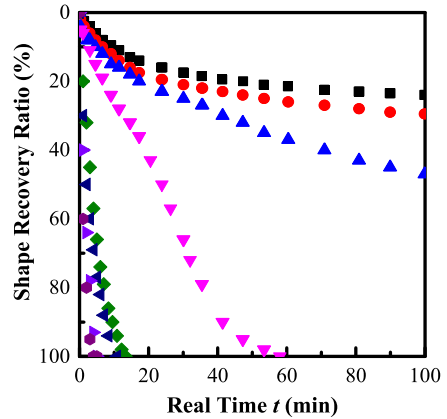
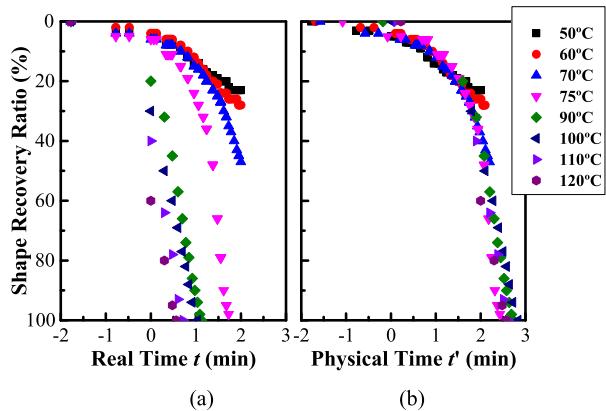


Fig. 13 (a) The recovery ratio curves and (b) the corresponding master curve. The reference temperature was 50 °C



recovered. As the initial deformation varied, it was difficult to evaluate accurately. The shape of the SMP eventually recovered over time as the temperature increased, demonstrating the time–temperature dependency.

To consider the time–temperature superposition principle of the material's shape recovery behavior, the horizontal axis of Fig. 12 was converted to a logarithmic scale, as shown in Fig. 13(a). The shapes of the shape recovery curves were similar. The curves were superimposed with respect to a reference temperature of 50 °C, resulting in a smooth master curve for the shape recovery, as shown in Fig. 13(b). The shift factors for the shape recovery behavior were obtained as shown in Fig. 14. Note that the shift factors differed from the time–temperature shift factors obtained in the creep tests; therefore, the time–temperature shift factors for both master curves showed different acceleration behavior. These differences were considered to resolve the error between the estimated and experimental data.

6 Estimation with the time–temperature shift factor for shape recovery

The shift factor difference discussed in the previous section was attributed to the differences in behavior under creep and shape recovery. The deformation behavior that occurred during the temperature variation period in the creep and recovery tests appeared to be dominated

Fig. 14 The time–temperature shift factor for shape recovery

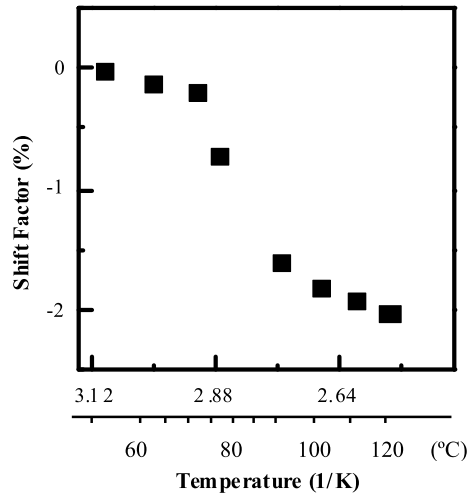
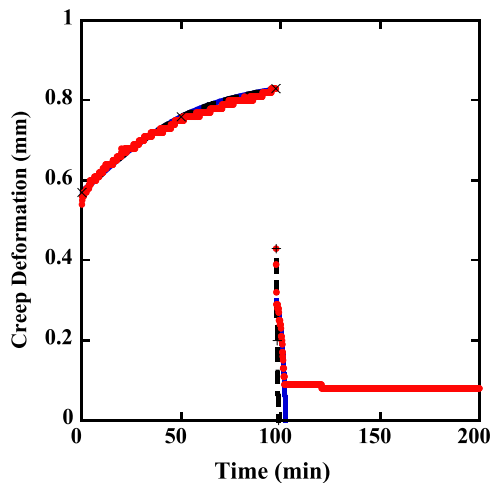


Fig. 15 A comparison between the experimental results and the estimated results using the time–temperature shift factor for the shape recovery behavior



by shape recovery. The estimated results using the time–temperature shift factor, shown in Fig. 15, were in good agreement with the experimental data, as opposed to the estimated results using the time–temperature shift factor from the creep tests. In the present study, no plastic deformation was considered; thus, there was the potential for overestimation in the creep and shape recovery results. Consequently, we clarified that the two-phase linear viscoelastic model could be applied to the polyurethane based SMP, that is, the estimation for the creep, creep recovery, and shape recovery above T_g on the SMPs, requires both creep and shape recovery data. The recovery behavior above T_g was dominated by the shape recovery behavior.

7 Conclusion

Creep, creep recovery, and shape recovery behaviors were investigated and evaluated using linear viscoelastic theory; the time–temperature superposition principle was applied to creep

and shape recovery behavior. In this estimation, creep and creep recovery were accounted for based on the linear viscoelastic theory; the estimations were in good agreement with the experimental results. However, the transition region with regard to temperature variation showed little correspondence due to the influence of viscoelasticity in the shape recovery behavior. The time–temperature superposition principle was applied to the shape recovery behavior, and a master curve for shape recovery and their time–temperature shift factors were obtained. A comparison of the time–temperature shift factors between creep and shape recovery differed, as evidenced by the slope of the shift. Using the shift factors for shape recovery, the estimation in the transition area of the load change agreed with the experimental data. Thus, two-phase linear viscoelastic model could be applied to the experimental results, that is, the estimation of the shape recovery requires information on the viscoelastic properties of the shape recovery behavior, with the recovery behavior above T_g being dominated by shape recovery by viscoelasticity.

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