

Characterization of Viscoelastic Behavior of Shape Memory Epoxy Systems

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ABSTRACT: Viscoelastic behavior has a remarkable impact on the functional realization of shape memory polymers and their composites. Our previous work reported that a series of shape memory epoxies with varied curing agents and contents were synthesized and exhibited higher shape fixture and recovery rates. The viscoelastic behavior of the materials at different temperatures is experimentally investigated in this study. Stress–strain hysteresis under uniaxial tension, stress relaxation, and creep tests are performed. The energy dissipation factor and residual strain factor as functions of temperatures are presented in the basis of stress–strain hysteresis tests. Moreover, the effects of test temperature, curing-agent type, and content on the viscoelastic behavior of these materials are discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Shape memory polymers (SMPs) present many unique advantages over traditional shape memory alloys and ceramics, for example, low density, high fixture strain, easy processing, wide shape transition temperature, and even biocompatibility.¹ During the last 2 decades, various novel SMPs and their composites have been reported, including SMP matrix,^{2–8} particle- or fiber-reinforced SMP composites,^{9–12} SMP foams,¹³ and sandwich structures.^{14,15} Meanwhile, enormous reports have been presented on thermomechanical properties of SMPs since heating is the primary stimulus for them to realize the shape memory effect.^{16–23}

Although extensive work has been performed on the thermomechanical behavior of SMPs, some issues remain unresolved. For example, as a class of semicrystalline polymers, SMPs exhibit viscoelastic response in the vicinity of the glassy transition temperature, T_g . However, until now most thermomechanical constitutive equations about SMPs are rate-independent, which is primarily due to few experiments performed on the viscoelastic response of SMPs.^{24,25} In this study, the viscoelastic behavior of four types of epoxy SMPs with different critical shape transition temperatures are investigated. The temperature impact on the viscoelastic response is discussed.

MATERIAL PREPARATION AND EXPERIMENTS

Shape memory epoxies are prepared by epoxy resin E-51 with varying the content of curing agents of 4,4'-methylenedianiline

(DDM) and *m*-phenylenediamine (*m*-PDA). The synthesis process has been described in Ref. 26. Here, we present a brief description as follows: After preheating to 110°C, epoxy resin E-51 is stirred for 20 min at the velocity of 150 r/min by a magnetic-force stirrer. Then, the presetting quantity of the curing agent is added and stirred for another 20 min at the velocity of 260 r/min. A homogenous solution is produced. After that, the solution is poured into a mold and dried for 2.5 h at 80°C and subsequently for 2.0 h at 150°C. Finally, four types of shape memory epoxy systems were synthesized. Table I lists the formulations of the specimens used in this study, and they are marked as 1# to 4#.

Our previous experiments have confirmed that these epoxy SMPs exhibit ideal shape memory effects.²⁶ Both the shape fixture rate at the room temperature and shape recovery rate at the high temperature for all investigated specimens are higher than 95%. In this study, the viscoelastic behavior of the materials at varied temperatures is investigated via three experiments: uniaxial tensile hysteresis test, stress relaxation, and creep tests. The experiments are performed by an in-house developed test system and a temperature-controlled environmental chamber. The size of the specimens is $50 \times 15 \times 3.34 \text{ mm}^3$ (length \times width \times thickness). A few thermal cycles are carried out before experiments, which could effectively eliminate the prefrozen strain accumulated during the fabrication process and obtain more agreeable experimental results. The temperature is measured by a thermocouple thermometer. To ensure temperature

Table I. Formulations of the Prepared Shape Memory Epoxy Systems (Mass Ratio)

Specimen	1#	2#	3#	4#
E-51	100	100	100	100
DDM	15	17	9	10.5
m-PDA	0	0	3.6	2.7

equilibrium in specimens, the specimens are kept more than 10 min before the experiment at every test temperature. Because the stiffness and limit strain of SMPs in the glassy and rubbery

states have about 2–3 orders change, the loading rate and maximum applied stress/strain amplitudes at different temperatures are different, but all results are obtained in the elastic deformation stage.

RESULTS AND DISCUSSION

Stress-Strain Hysteresis

Because of the viscoelastic response, polymers and matrix-dominated polymeric composites usually exhibit a phase lag between the strain and stress during the loading process, which causes the formation of the hysteresis curve even if the applied stress level is much lower than the material's yielding stress. Hysteresis

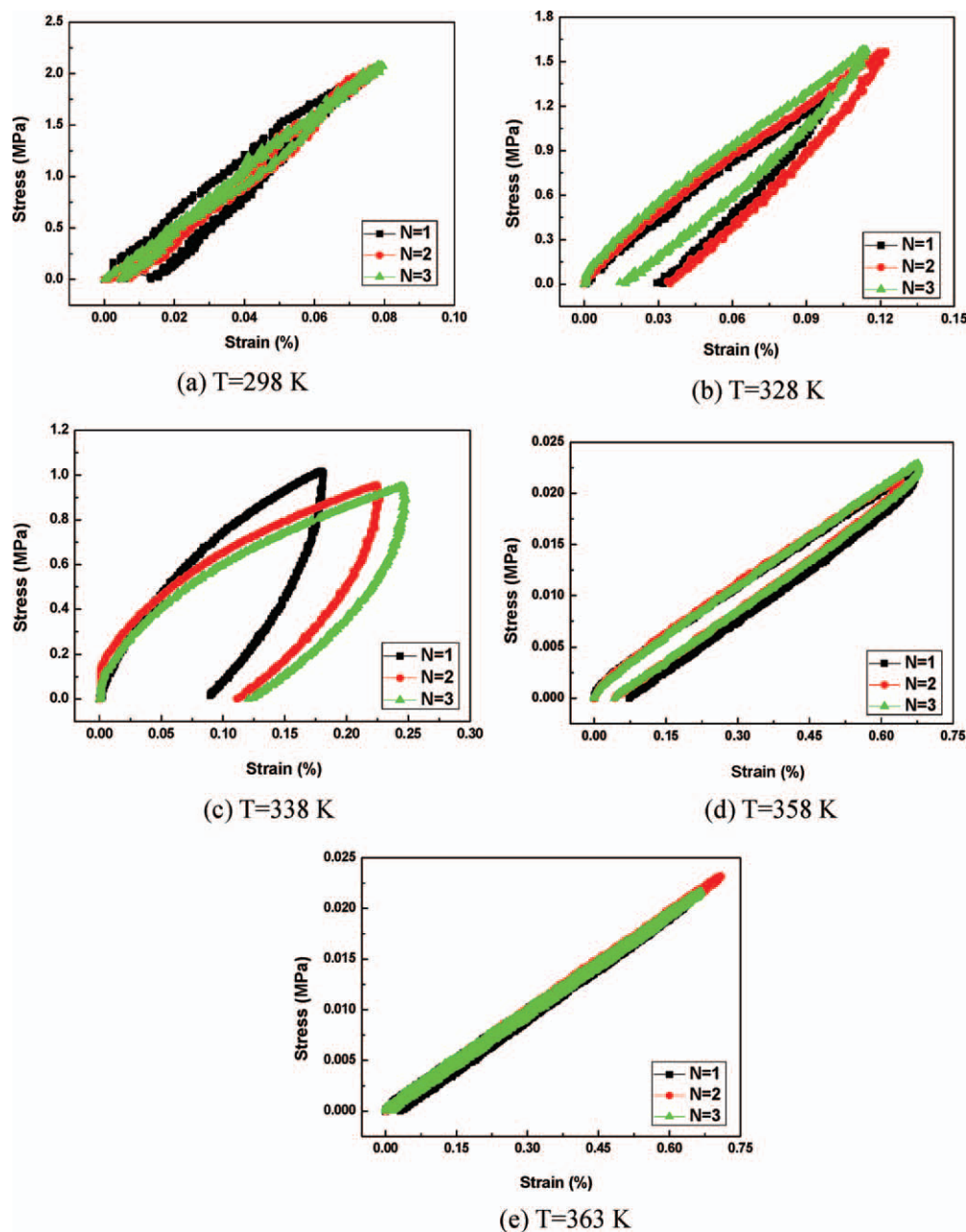


Figure 1. Typical hysteresis curves of the shape-memory epoxy at different temperatures. Noted that different maximum stress/strain amplitudes were applied at different temperatures because the elastic limit of SMPs in the glassy and rubbery states have about 2–3 orders change. Similar considerations were put in the following stress relaxation and creep tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

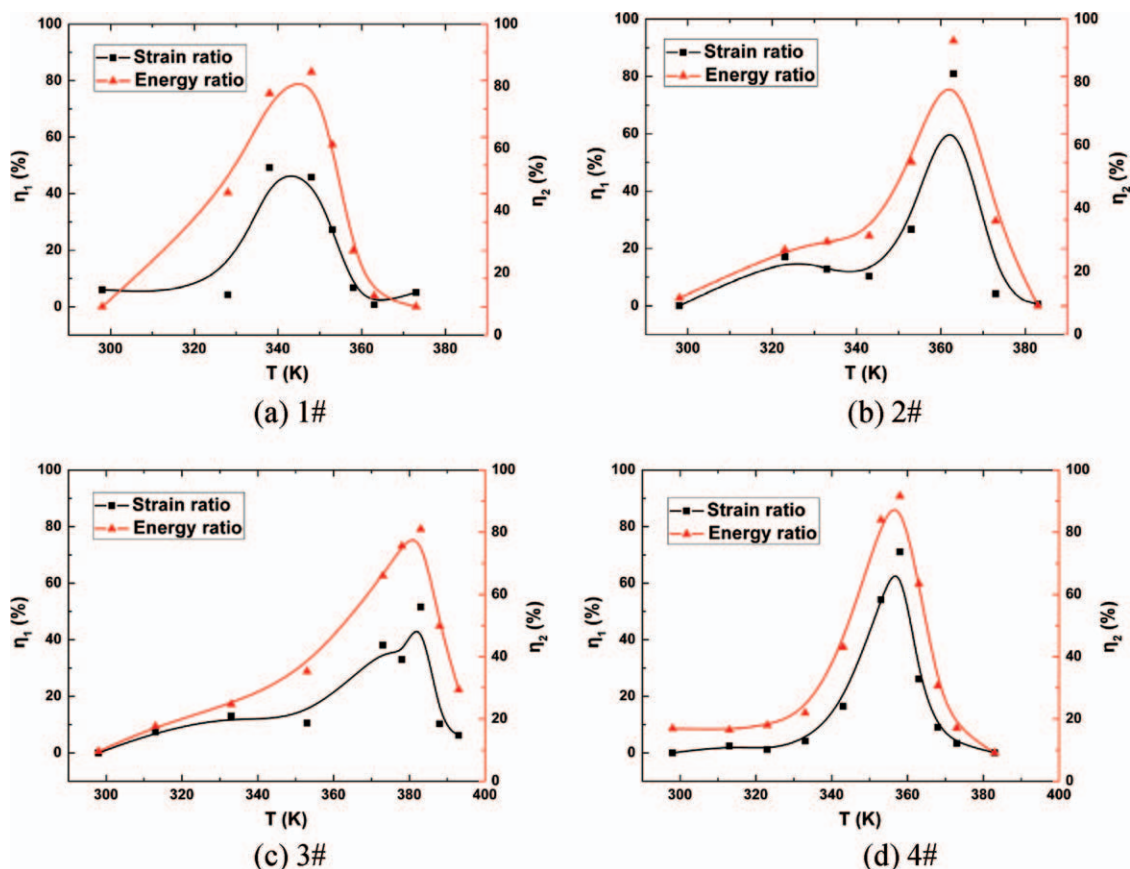


Figure 2. Variations of η_1 and η_2 on temperatures for shape-memory epoxies. The results are obtained by the third stress–strain hysteresis curve at every temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curves can provide lots of information, for example, cyclic softening/hardening, storage and loss energies, material damping, and cyclic creep behavior.^{27,28}

Figure 1 presents the test results of typical stress–strain hysteresis curves of the shape memory epoxy at different temperatures. The experiments are repeated three times at every temperature. The different dependences of stress–strain hysteresis on temperature are due to the phase change of the shape memory epoxy from the low temperature to high temperature. When the temperature is much lower than T_g of the material, the specimen is in the glassy state and the applied stress causes a change in the internal energy. When the temperature increases well above T_g of the material, the specimen is in the rubbery state and the applied stress produces a change of the conformational entropic state of the polymer chains. In both glassy and rubbery states, the elastic strain can be stored and released instantaneously, and the viscosity is relatively small and can be neglected [Figure 1(a, e)]. However, the remarkable phase lag between the strain and stress exhibits in the middle transition region because the viscoelasticity governs the deformation and recovery of the shape memory epoxy in this stage [Figure 1(b–d)].

The residual strain after a stress–strain loop in Figure 1 reflects the viscoelastic effect of the material, and the enclosed area of the stress–strain hysteresis reflects the energy dissipation. In this study, two viscoelastic factors, η_1 and η_2 , are, respectively, defined as

$$\eta_1 = \frac{\varepsilon_{\text{residual}}}{\varepsilon_{\text{max}}}, \quad \eta_2 = \frac{E_{\text{loss}}}{E_{\text{total}}}, \quad (1)$$

where, $\varepsilon_{\text{residual}}$ and ε_{max} represent the residual strain and the maximum strain in the stress–strain hysteresis, respectively; E_{loss} and E_{total} denote the loss energy and total energy in the stress–strain hysteresis, respectively. Figure 2 shows the dependence of η_1 and η_2 on temperature. The results are determined by the third stress–strain hysteresis curve at every temperature. Similar results can also be obtained by the first and second loading cycles. With decreasing temperature, both η_1 and η_2 increase gradually at the low temperature. After reaching the maximum values, both η_1 and η_2 decrease quickly with further increasing the temperature. The result indicates that the viscoelastic behavior of the materials is not symmetric with the temperature, and the influence at the low temperature is more remarkable than that at the high temperature. Moreover, although the physical definitions are different, the influences of η_1 and η_2 on temperature are similar, and they reach the peak value nearly at the same temperature for the same material.

Stress Relaxation

In addition to the stress–strain hysteresis, stress relaxations of the specimens at different temperatures were also performed. Figure 3 presents some typical test results. When the temperature is much lower or well above T_g [Figure 3(a, c)], the stress

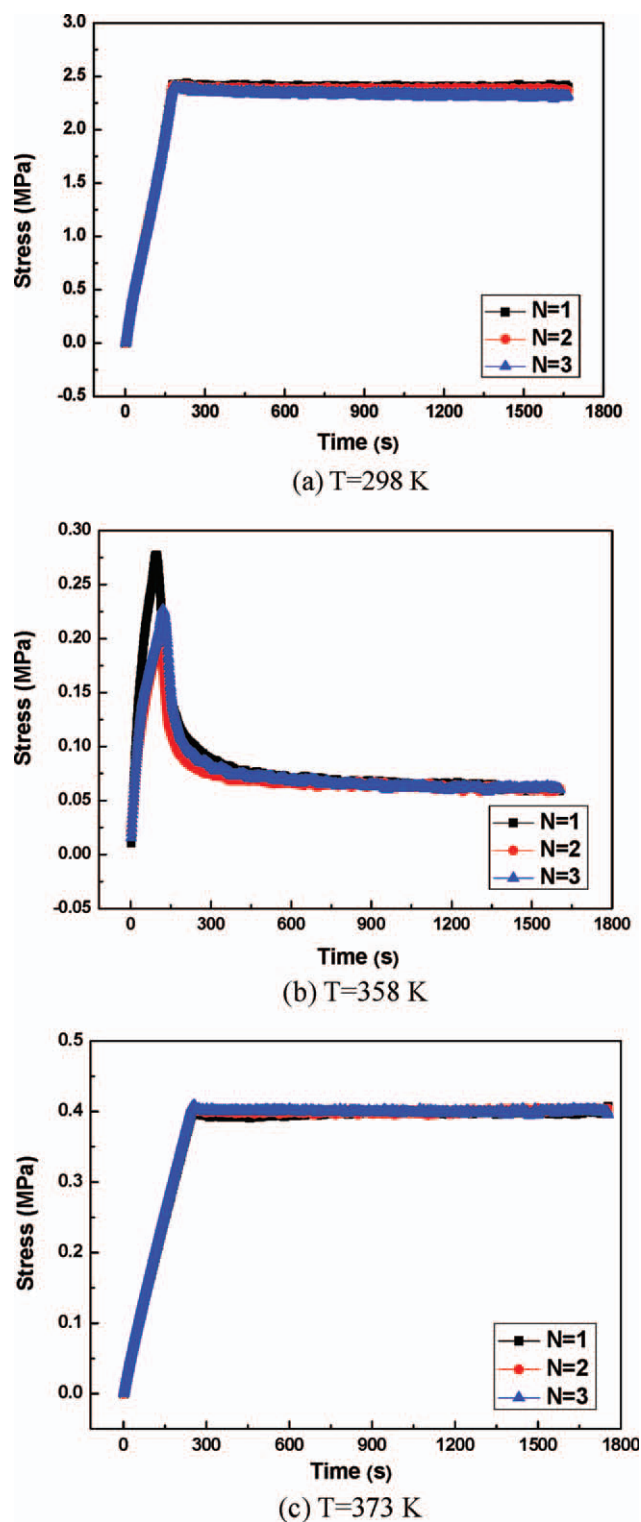


Figure 3. Typical stress relaxation curves of epoxy SMP at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

relaxation is very small and could be neglected. During the glassy transition region [Figure 3(b)], the material exhibits remarkable nonlinear stress relaxation behavior: quick stress

decrease at the primary stage, and then gradual decrease in the second stage. The deformation mechanisms of semicrystalline polymers in these two stages are different. The primary stress relaxation is resulted from the elastic deformation and viscous or orientated flow of amorphous polymer chains in the short-term, and the second is associated with the damage from crystallized polymer or oriented non-crystalline regions.²⁷ In the microstructure view, SMPs are the coexistence of the crosslinked stable segment and the reversible switched segment.²⁹ The cross-linked stable segment is deformed elastically and insensitive to the temperature. The reversible switched segment, however, exhibits high viscoelastic behavior during the glassy transition region. Thus, the first stress relaxation stage in Figure 3(b) is dominated by the viscous flow of the reversible switched segment, and the second stage is determined by the damage of crosslinked stable segment and reversible switched segment. Because the applied pre-stress in this study is much lower than the material's yielding stress, the stress relaxation rate in the second stage is small.

Figure 4 shows the relative stress decay with the loading time for specimens 1# to 4# at different temperatures, which are determined by the instantaneous stress divided by the initial applied stress. To present a clear view of the test results, Figure 5 shows the relaxation ratios of the four types of specimens when the relaxation time is 1200 s. The relaxation ratio at any time, $R_{\text{relaxation}}(t)$, is expressed as

$$R_{\text{relaxation}}(t) = \frac{\sigma_{\text{pre}} - \sigma(t)}{\sigma_{\text{pre}}} \quad (2)$$

where, σ_{pre} and $\sigma(t)$ denote the pre-stress and the instantaneous stress during the experiment.

According to Figures 4 and 5, the maximum stress relaxation temperature of specimen 2# with 17% DDM curing agent is much higher than that of specimen 1# with 15% DDM curing agent, which indicates that a higher content of the curing agent could improve the T_g and change the viscoelastic region in SMPs. In addition, although the total curing agent content of specimen 3# with 9% DDM and 3.6% m-PDA is the lowest in all specimens, its peak stress relaxation temperature is the highest. The lower T_g of specimen 4# may be due to the too much lower ratio of m-PDA to DDM. Thus a higher T_g might be obtained using suitable ratio of mixed curing agents. The results in Figures 4 and 5 confirm that it is possible to obtain tailored viscoelastic responses in shape memory epoxies by changing the content and type of curing agents.

Creep Deformation

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 leads to the creep fracture of the structure. Hence, it is of great importance to know about the creep properties and improve the creep resistance of polymers and their composites.

Figure 6 shows the creep deformation of specimens 1# to 4# at different temperatures, where the creep ratio is defined as the instantaneous creep strain divided by the initial applied strain.

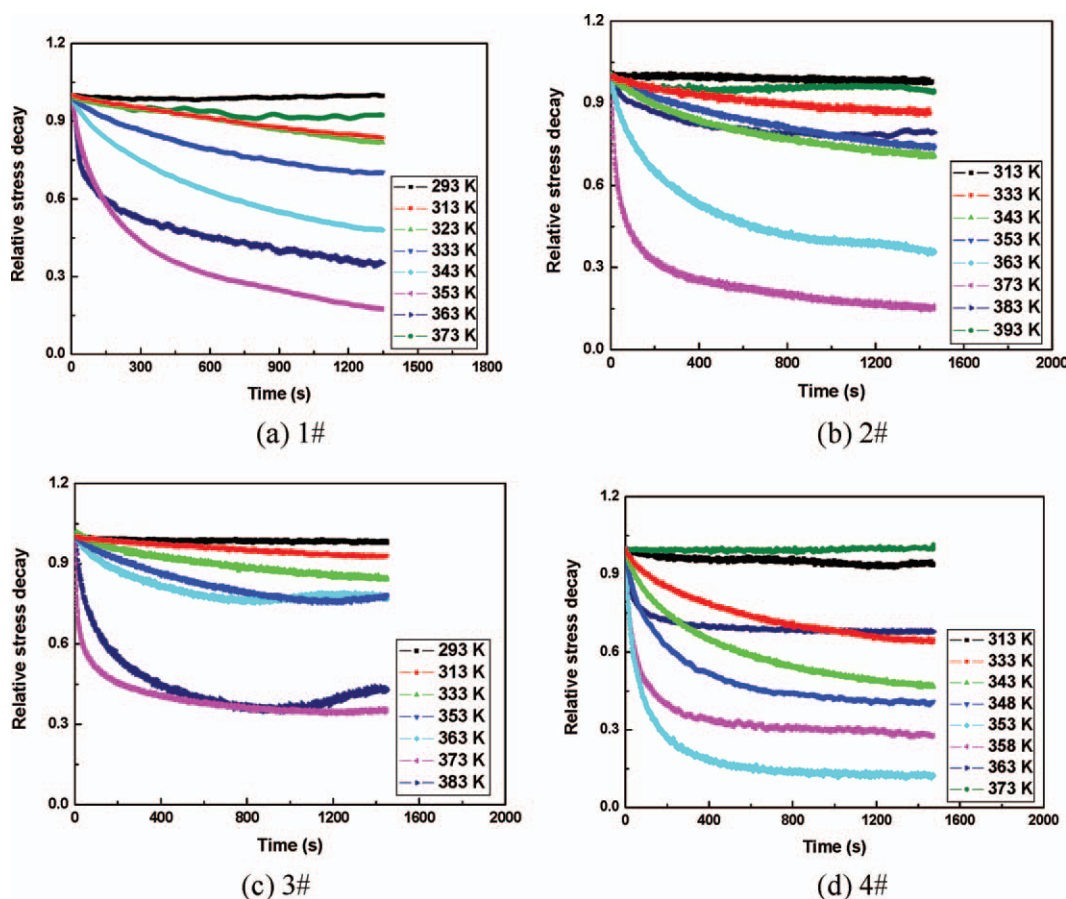


Figure 4. Curves of relative stress decay versus time of specimens 1# to 4# at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the test result, the maximum creep ratios of specimens 1# to 4# are 3.23, 7.44, 4.01, and 4.42. Since the total creep time in this study is lower than 1500 s, the creep behavior of specimens 1# to 4# is remarkable in the glassy transition region. We know that the shape transition response of SMPs is also located in the glassy transition region, thus the viscoelastic effect will have a great impact on the function realization of SMPs. Moreover, Figure 7 shows the creep ratios of the four types of specimens when the relaxation time is 1200 s, which presents a more clear insight about the creep behavior of the specimens at different temperatures.

The shape memory effect of SMPs is due to the frozen of segment chains at low temperatures and subsequently recovery at elevated temperatures. The critical transition temperature, T_{tran} , is defined by the temperature where the shape transition rate reaches the highest, which is one of the most important parameters in characterizing the shape memory effect of SMPs. Because the shape memory of SMPs is due to the glassy transition, T_{tran} is usually regarded as T_g . However, it is not easy to be accurately measured in experiments. For example, the critical shape recovery temperature reported in Ref. 18 is about 10 K higher than the critical shape recovery value for the same shape memory epoxy. Our previous study²⁶ confirmed that there had up to about 20 K of difference to determine T_{tran} -values by dif-

ferential scanning calorimetry, dynamic thermomechanical analysis, and shape recovery tests. The reason is that the viscoelastic effect in different tests is different. Figure 8 shows the T_{tran} -values of specimens 1# to 4# determined by the stress-strain

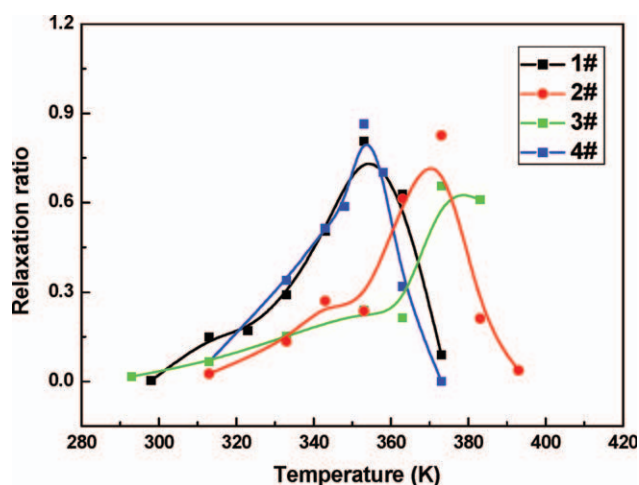


Figure 5. Stress relaxation ratios of shape memory epoxies at different temperatures ($T = 1200$ s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

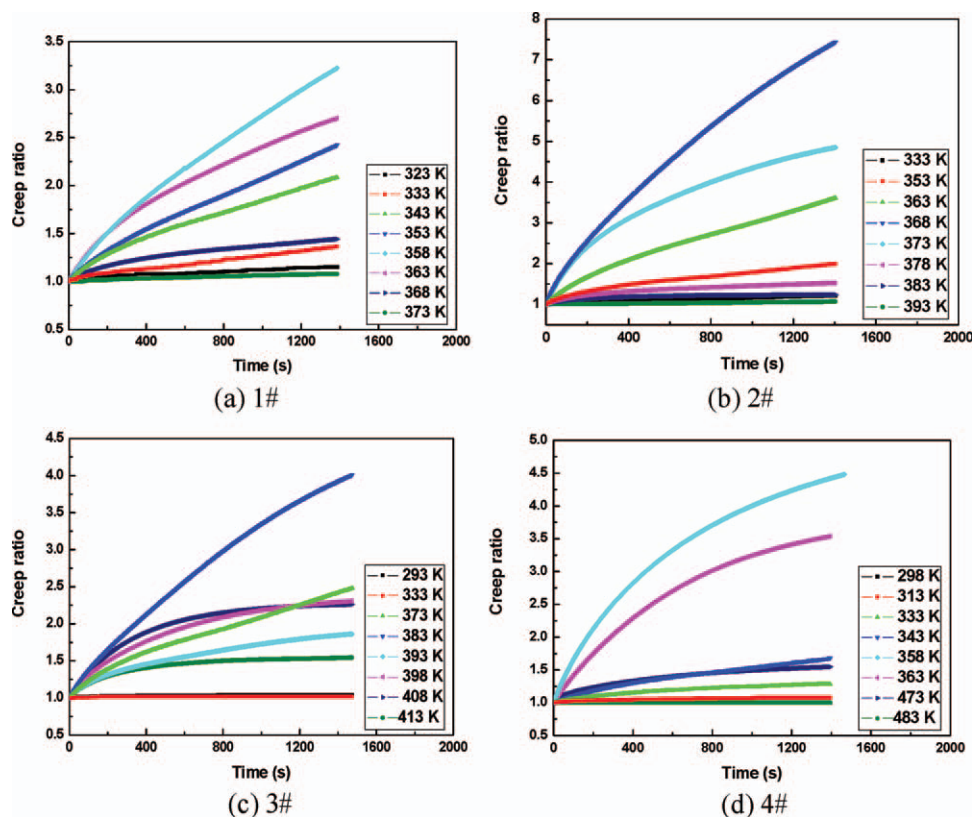


Figure 6. Creep curves of the shape memory epoxies at different temperatures. The creep ratio is defined as the instantaneous creep strain divided by the initial applied strain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hysteresis, stress relaxation, and creep tests. It is interesting to find that the T_{tran} -values determined by these three experiments are well agreeable. The result is easy to be understood because the viscoelastic effect in these experiments is fully considered. Therefore, Figure 8 presents a clue how to determine the T_{tran} -value of SMPs more accurately.

CONCLUSIONS

The viscoelastic behavior of a series of epoxy SMPs at different temperature was experimentally investigated. The stress-strain hysteresis under uniaxial tension, stress relaxation, and creep tests were performed. The results confirm that the viscoelastic effect is much small at lower and higher temperatures, but

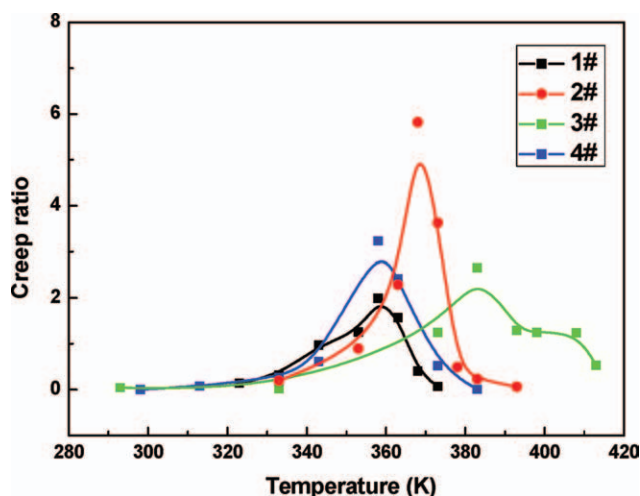


Figure 7. Curves of creep ratios versus temperatures for specimens 1# to 4#. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

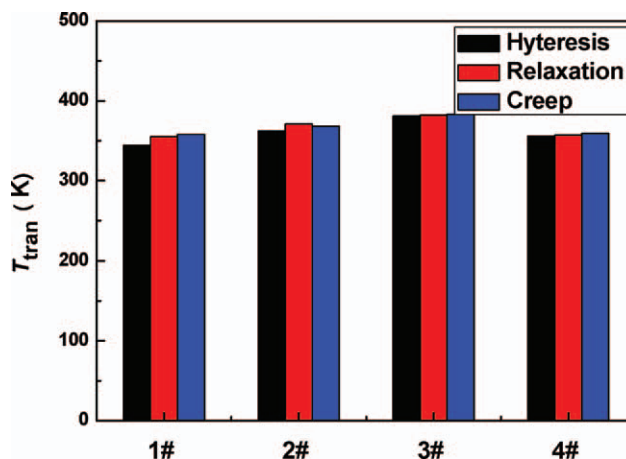


Figure 8. Comparison of T_{tran} -values determined by different tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

remarkable in the glassy transition region. A higher peak transition temperature can be obtained by increasing content of curing agents or using suitable mixed curing agents. In addition, the critical shape transition temperatures determined by the stress-strain hysteresis, stress relaxation, and creep tests are well in agreement.

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