# Shape-Memorized Crosslinked Ester-Type Polyurethane and Its Mechanical Viscoelastic Model

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ABSTRACT: A series of shape-memorized crosslinked ester-type polyurethanes (PUs), based on different compositions of 4,4'-diphenyl methane diisocyanate (MDI), poly(butylene adipate) glycol (PBAG) with different molecular weight (MW) and trimethylol propane (TMP), were synthesized. The morphology of samples was investigated by using DSC, WAXD, and dynamic mechanical analysis (DMA). It was found that the morphology of the soft segment, which was PBAG with a different MW, was in an amorphous state and no crystalline domain was found. By increasing the crosslinked density (varying the content of TMP) or decreasing the length of the soft segment (MW of PBAG), the glass transition temperature of studied samples increased. But the range of transition broadened and the modulus ratio  $E'_{(T_g-20^{\circ}\mathrm{C})}/E'_{(T_g+20^{\circ}\mathrm{C})}$  also decreased. The shape-memory behavior was studied by the bending test method adopted from the shape-memory alloy. The sample with high  $T_g$  showed not only a high recovered temperature  $(T_r)$  but also a high recovered rate  $(V_r)$  with a high modulus ratio. By introducing the chemical crosslinked structure, the deformed samples completely recovered their original shape and rendered shape-memory behavior under the complex deformation. The shape-memorized crosslinked ester-type PUs can be applied at different operating temperatures. A mechanical viscoelastic model is discussed for the shape-memory behavior of PUs, and the modified Bonart's viscoelastic model properly describes the mechanism of the shape memory of PUs. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1305-1319, 1999

**Key words:** Crosslinked ester-type polyurethanes; shape memory behavior; molecular morphology; mechanical viscoelastic model

# **INTRODUCTION**

Shape-memory polymers are functional materials that are able to fix a deformation, by hardened reversible phase, without external force for a long time; they are also able to recover their original shape, by fixed phase, after heating.<sup>1,2</sup> Hence, the reversible phase should show a low phase-transition temperature  $(T_L)$ .<sup>1,2</sup> After cooling below  $T_L$ 

and releasing the external force, the deformation of the shape-memory polymers can be fixed because this hardened state resists the elastic recovered force of the fixed phase. The fixed phase was the entanglement of a polymeric chain, the chemical crosslinked point, or the physical crosslinked point with a high characteristic temperature  $(T_H)$ . The reversible phase, on the other hand, is softened by heating. The deformed polymer can recover its original shape by the elastic recovered force of the fixed phase.

For practical applications, the phase-transition temperature of shape-memory polymers was a

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Materials	Fixed Phase	Reversible Phase
Trans polyisoprene <sup>a</sup>	Chemical crosslinked point	Low $T_m$ of the crystal
PS-PB copolymer <sup>b</sup>	High $T_g$ of PS	Low $T_g$ of PB
Segmented PU <sup>c</sup>	High $T_g$ or $T_m$ of Hard segment	Low $T_g$ or $T_m$ of Soft segment
Polynorbornene <sup>d</sup>	Entanglement of molecular chain	Glass state of molecular chain

Table I The Morphology and Application of Polymers

<sup>a</sup> See Ref. 1.

<sup>b</sup> See Ref. 4. <sup>c</sup> See Ref. 3.

<sup>d</sup> See Ref. 5.

little higher than the operating temperature. Their properties were different from those of traditional polymers; hence, several kinds of polymers, listed in Table I,<sup>1-5</sup> with shape-memory properties demonstrated in various applications were researched in industry laboratories to extend the applications of traditional polymers.

In recent literature, Takashi et al. and Hayashi et al. have studied the thermal structure and dynamic mechanical properties of two series of segmented polyurethanes (PUs) with shape-memory behavior.<sup>6-9</sup> Kim et al. and Li et al. have studied the effect of crystallization of polycaprolacton (PCL), as the reversible phase, on shapememory behavior.<sup>10-12</sup> Hirai et al. have studied the influence of chemical crosslinked structures on the shape-memory behavior of poly(vinyl alcohol) hydrogel.<sup>13,14</sup> Li has introduced the structure of interpenetrating polymer networks (IPNs) to shape-memorized polyacrylamide.<sup>15</sup> In our previous study, the influences of hard segment content<sup>16</sup> and soft segment molecular weight (MW)<sup>17</sup> on the shape-memory behavior of polyether-based PUs were studied.

In this study, a series of crosslinked ester-type PUs with different composition were synthesized by poly(butylene adipate) glycol (PBAG), 4,4'-diphenyl methane diisocyanate (MDI), and trimethylol propane (TMP) to study the relationship among the morphology, viscoelastic properties, and shape-memory behavior. The fixed phase was the chemical crosslinked point (TMP), and the reversible phase was the soft segment (PBAG) with different length of molecular chain. The mechanical viscoelastic description of the shapememory process was given first, modified by Bonart's viscoelastic model<sup>18</sup> of segmented PUs. The morphology of specimens was studied by using differential scanning calorimetry (DSC) and wideangle X-ray diffraction (WAXD). The dynamic properties were investigated by using dynamic

mechanical analysis (DMA) in the tensile mode. The shape-memory behavior of studied PUs was observed by the bending test method, which was adopted from that of shape-memory alloy.<sup>19</sup> The experimental process was discussed and the data analysis was performed for the experiments carried out. The results were discussed and, finally, conclusions were given.

# MECHANICAL VISCOELASTIC MODEL

The viscoelastic properties of polymers would not properly be described by the spring or the dashpot; thus, the Maxwell model and the Voigt model were proposed to describe the mechanical behavior of polymers. Furthermore, several generalized models were proposed to explain the mechanical response of the polymer with two transitions. One was the Maxwell-Wiechert model,<sup>20</sup> a generalized Maxwell model that consisted of an arbitrary number of Maxwell models connected in parallel. The other was the Voigt–Kelvin model,<sup>21</sup> a generalized Voigt model that consisted of an arbitrary number of Voigt models connected in series. As mentioned previously, the morphology of shape-memory polymers was composed of the fixed phase and the reversible phase, but with a substantial difference in their characteristic temperatures; that is, the phase transition of the reversible phase was at a low temperature but that of the fixed phase was at a high temperature. On the basis of segmented PUs, Bonart<sup>18</sup> has proposed a mechanical model like the Maxwell-Wiechert model to characterize the segment mobility and the crosslinking stability of molecular morphology. Consequently, for shape-memory polymers, a viscoelastic model, consisting of two Maxwell models connected in parallel, was proposed. These two Maxwell models represented reversible phase and fixed phase, respectively, as



**Figure 1** The viscoelastic model and mechanism of shape-memory polymer: (a) the general model of shape-memory polymer; (b) the simplified model of the crosslinked shape-memory polymer; (a-1) deformed to  $\varepsilon_0$  at  $T_1$ ; (a-2) kept the strain  $\varepsilon_0$  at  $T_1$  for a long time, then cooled to  $T_2$ , followed by a release of the external force; (a-3) heated at the rate of  $T = T_2 + at$  and, after heating, the model recovers to its original state.

shown in Figure 1(a). The mechanical behavior and the mechanism of the shape-memory behavior of the viscoelastic model were described as follows.

At a high temperature (e.g.  $T_L < T_1 = 80^{\circ}\text{C} < T_H$ ), the model was stretched to a constant strain  $\varepsilon_0$  and maintained this constant strain as shown in Figure 1(a-1). Based on the relaxation experiment, the mechanical parameters of the model were derived as a function of time (t) and temperature (T). The modulus E(t, T) and stress  $\sigma(t, T)$  of the model, obtained from the relaxation test, are expressed as follows<sup>22</sup>:

$$E(t, T) = E_{f}(T) \times \exp[-t/\tau_{f}(T)] + E_{r}(T)$$
$$\times \exp[-t/\tau_{r}(T)] \quad (1)$$

$$\sigma(t, T) = \varepsilon_0 \times [E_f(T) \times \exp[-t/\tau_f(T)] + E_r(T) \\ \times \exp[-t/\tau_r(T)]] \quad (2)$$

The subscripts f and r indicate the fixed phase and reversible phase, respectively, and E indicates the modulus of spring within the Maxwell model. The relaxation time  $\tau$  is defined as

$$\tau_i = \frac{\eta_i}{E_i} \tag{3}$$

The subscript *i* indicates *f* or *r* and  $\eta$  indicates the viscosity of dashpot within the Maxwell model. Hence, the strains of the elements in the viscoelastic model were obtained as follows:

$$\varepsilon'_{f}(t, T) = \varepsilon_{0} \times \exp[-t/\tau_{f}(T)]$$
 (4)

$$\varepsilon_f'(t, T) = \varepsilon_0 \times (1 - \exp[-t/\tau_f(T)])$$
(5)

$$\varepsilon'_r(t, T) = \varepsilon_0 \times \exp[-t/\tau_r(T)]$$
 (6)

$$\varepsilon_r''(t, T) = \varepsilon_0 \times (1 - \exp[-t/\tau_r(T)])$$
(7)

where  $\varepsilon'$  and  $\varepsilon''$  are the strain of spring and dashpot, respectively.

At this temperature  $(T_1)$ , the value of modulus and viscosity of the reversible phase used in Maxwell model were low. Hence, by keeping the strain at  $T_1$  for a long time  $(t_{\infty})$ , the model shifts to a steady state, the value of  $\varepsilon''_r$  approaches  $\varepsilon_0$ , and the value of  $\varepsilon'_r$  shifts to zero; however,  $\varepsilon'_f$  and  $\varepsilon''_f$ contributed to the same strain  $(\varepsilon_0)$  in the fixed phase's Maxwell model. The relationship between these strains is expressed as

$$\varepsilon_0 = \varepsilon_f' + \varepsilon_f'' = \varepsilon_r'' \tag{8}$$

At this stage, the mechanical response involved only the deformed spring and dashpot of the fixed phase's Maxwell model and the deformed dashpot of the reversible phase's Maxwell model. Then, this system was maintained at that constant strain and cooled to a low temperature (e.g.  $T_2 = -20$  °C  $< T_L$ ).

The operating temperature was far from the characteristic temperature of the fixed phase, thus, the values of  $E_f$  and  $\eta_f$  can be thought of as

constants under the temperature range of operation.

Under the condition of no external force loading and at the low temperature  $(T_2)$ , the viscid fluid (dashpot) could not render mechanical response. Hence, the strain of the dashpot of the fixed phase's Maxwell model  $(\varepsilon_{f})$  would not change anymore and can be obtained by eq. (4).

$$\varepsilon_{f}^{\prime\prime}(t_{\infty}, T_{1}) = \varepsilon_{0} \times (1 - \exp[-t_{\infty}/\tau_{f}(T_{1})]) \quad (9)$$

The other strain of elements can also be obtained

$$\varepsilon_{f}'(t_{\infty}, T_{1}) = \varepsilon_{0} \times \exp[-t_{\infty}/\tau_{f}(T_{1})] \qquad (10)$$

$$\varepsilon_r''(t_\infty, T_2) = \varepsilon_0 \tag{11}$$

On the other hand, the total stress was zero. Consequently,

$$\sigma_f + \sigma_r = 0 \tag{12}$$

where  $\sigma_f$  indicates the recoverable stress of the deformed spring of the fixed phase's Maxwell model and  $\sigma_r$  is the resisted stress of the deformed dashpot of the reversible phase. With Hook's law and Newton's law, eq. (12) is represented as follows:

$$E_f imes \varepsilon'_f + \eta_r(T_2) imes rac{d \varepsilon''_r}{dt} = 0$$
 (13)

Equation (13) was rearranged and the strain rate  $d\varepsilon''_{l}/dt$  was obtained as

$$\frac{d\varepsilon_r''}{dt} = -\frac{E_f \times \varepsilon_f'}{\eta_r(T_2)} \tag{14}$$

Equation (14) can be used to understand whether the deformation of the shape-memorized viscoelastic model can be fixed; that is, if the viscosity  $\eta_r(T_2)$  was large, the strain rate would be reduced to a small value, even to zero. Hence, the strain of the model would not be changed at the low temperature  $(T_2)$ . The hardened reversible phase might effectively fix the deformation to resist the elastic recovery of the fixed phase.

The viscosity of the dashpot of the reversible phase's Maxwell model is reduced during the heating process, and the strain rate increases with a decrease in viscosity  $\eta_r$ . When the factor of fixing deformation disappears, the deformed

Table IIThe Notation and Molar Ratio ofMonomers of the Studied PUs

Notation <sup>a</sup>	MDI : PBAG : TMP
A1, B1, C1	2:1:2/3
A2, B2, C1	4:1:2
A3, B3, C3	6:1:10/3
A4, B4, C4	8:1:14/3
A5, B5, C5	10:1:6
A6, B6, C6	12:1:22/3

<sup>a</sup> A, B, C indicated that the different MW of PBAG were used. A: MW of PBAG was 1000; B: MW of PBAG was 2000; and C: MW of PBAG was 2800; e.g. A1: MDI : PBAG : TMP = 2 : 1 : 2/3, and MW of PBAG was 1000.

model recovers for the spring element in the fixed phase's Maxwell model, as shown in Figure 1(a-3). Finally, the model recovered to its original state as shown in Figure 1(a). Consequently, this viscoelastic model describes the mechanism of the shape-memory process quite well.

## **EXPERIMENTAL**

#### Materials and Preparations of PUs

Crosslinked ester-type PUs were synthesized in two steps. One mole of dehydrated PBAG was reacted at 70°C for 2 h, at first, with 2 mole MDI. Then, the NCO-terminated prepolymer was mixed completely with the curing agent, TMP, and molded on a plate at 80°C for 4 h. Finally, the molded samples were postcured at 130°C for 1 h. Samples of different soft segment (PBAG) lengths and crosslinked densities (varying content of TMP) were synthesized as listed in Table II.

#### **Characterization of Shape-Memory Polymers**

The thermal properties of the crosslinked estertype PUs were measured by using a TA9900 thermal analyzer with a DSC module. The environment of the measured samples was purged by nitrogen gas, then quenched with liquid nitrogen. DSC was carried out over a temperature range from -70 to 250°C at a heating rate of 10°C/min.

The wide-angle X-ray diffraction method was employed for studying the phase morphology by using a Philip PW 1710 at 30 kV and 20 mA. WAXD studies were carried out with samples of 1-mm thickness and with Bragg's angle  $2\theta$  from 5 to 60° at the rate of 3°/min.



**Figure 2** Schematic illustration of the shape-memory behavior with bending test used in this study.

Dynamic mechanical properties of the molded samples were determined by using a DuPont 983 DMA in the tensile mode at 1 Hz, 2°C/min. The glass transition temperature corresponded to the temperature of the peak-of-loss modulus curve. The modulus ratio was obtained by the definition  $E'_{(T_g-20^{\circ}\text{C})}/E'_{(T_g+20^{\circ}\text{C})}$ ,<sup>3</sup> where E' was the storage modulus. In the relaxation mode of DuPont 983 DMA, the relaxation test was performed with a constant strain of 50%; the test temperatures were the  $T_g$ 's of the sample at 0, 40, and 80°C.

The method of evaluating the shape-memory behavior of the shape-memory alloy<sup>19</sup> was adopted to investigate the shape-memory behavior of crosslinked ester-type PUs. The shapememory behavior was examined by a bending mode, as shown in Figure 2. The samples were deformed to an angle  $\theta_i$  at a bending temperature  $(T_b)$  above the  $T_g$  of the samples (e.g.  $T_b = 80$  °C) and kept for a constant bending time ( $t_b = 1$ min). Subsequently, the deformed samples were guickly cooled to a temperature lower than the  $T_{a}$ of samples (e.g.  $-20^{\circ}$ C) under constrained conditions with constant deformation for 1 min, followed by a release of the external force. Finally, the deformed samples were heated by a fixed heating rate (2°C/min). The change of  $\theta_f$  with temperature was recorded. The recoverable ratio [defined as  $(\theta_i - \theta_f)/\theta_i \times 100\%$ ] versus temperature was measured.

#### **RESULTS AND DISCUSSION**

#### Thermal Properties and Morphology of the Shape-Memorized Crosslinked Ester-Type PUs

Figure 3 shows the DSC scanning curves of samples with different lengths of soft segment (PBAG) and crosslinked densities (varying content of TMP). The crystalline domain of PBAG, with different MW, melted at about 45-60°C; however, the reacted PBAG could not crystallize in the crosslinked structure of PUs, whereas the melting behavior of crystal was not found on DSC scanning curves. During the heating process, the molecular chain of PBAG acted as amorphous only during the transfer from the glassy state to the rubbery state. These results were also examined by WAXD scanning, as shown in Figures 4-6. Pure PBAG (PBAG1000, PBAG2000, and PBAG2800), which did not react with MDI and to which no crosslinked structure was introduced. showed peaks as well-defined as the diffraction profile of WAXD. However, the diffraction profiles of the crosslinked ester-type PUs showed a broad shoulder for PBAG-based crosslinked PUs. Therefore, the results of DSC and WAXD implied that the crystallization of the soft segment, PBAG, was disturbed by the crosslinked structure. Consequently, the soft segment of the studied specimens acted as the glassy state at low temperature.

The sample with a high content of TMP implied that its crosslinked density was high in molecular structure. Figure 3 also shows that if more TMP is introduced, the broader will be the glass transition range of samples with the same length of soft segment. The introduction of TMP to form crosslinked structures not only disturbed the crystallized behavior of PBAG but also influenced the glass transition process. That effect was found from the DSC scanning in Figure 3. The transition range, dependent on temperature, was broadened when the crosslinked density (varying content of TMP) was increased; it meant that TMP acted as the fixed point. It constrained the mobility of the molecular chain of PBAG; therefore, the more TMP was used, the more energy was needed for PBAG to move and a higher  $T_{\sigma}$  of the studied PU was found. At the same time, the range of glass transition was also extended to high temperature; this broadened temperature range became unclear.

### Dynamic Mechanical Properties of Shape-Memorized Crosslinked Ester-Type PUs

Figures 7–9 show the DMA results, tensile storage modulus (E'), and tensile loss modulus (E'')of the three series of crosslinked PUs that are based on the different lengths of soft segment (PBAG) and content of TMP. Modulus ratio data



**Figure 3** The DSC scanning curves of PUs, based on different composition of monomers and MW of PBAG, MW = (a) 1000, (b) 2000, and (c) 2800.

are summarized in Table III. The glass transition temperature  $(T_g)$  of samples increased with increasing content of TMP, as shown in the results of DSC. The modulus of the glassy state of all samples, due to the elastic energy combined from crystalline and amorphous forms of the soft segment, showed similar values. This result indicates that the soft segment samples were no different from others in the low-temperature state. If the soft segment PBAG could crystallize, it would show a different modulus value with each different degree of crystallization at low temperatures.<sup>11</sup> Hence, the soft segment (reversible phase) of the studied samples was in the glassy state; studies of DSC and WAXD yielded the same results. However, an increase of crosslinked density (varying content of TMP) resulted in an increase of the rubbery state modulus, whereas the modulus ratio decreased. The rubbery state rendered enough strength at temperatures higher than  $T_g$  and provided enough force to recover the deformation.

Considering the same composition with the different MW of PBAG, the effect of the length of the soft segment was found, as shown in Figure 10. The  $T_g$  of PUs decreased with an increase of the length of the soft segment. The molecular chain of amorphous PBAG was more flexible than that of crystalline PBAG; both contributed the same effect on the strength at low temperature, but the longer flexible molecular chain of PBAG reduced the strength of the rubbery state at high temperature. Hence, the modulus ratio increased with an increase of the length of the soft segment (PBAG).



Figure 4 The WXAD profiles of PBAG-based (MW = 1000) PUs and pure PBAG 1000.

#### **Shape Memory Behavior**

DSC, WAXD, and DMA measurements of several samples were carried out for investigating the relationship between shape-memory behavior and the morphology of crosslinked ester-type PUs. The experimental results are shown in Fig-



Figure 5 The WXAD profiles of PBAG-based (MW = 2000) PUs and pure PBAG 2000.



Figure 6 The WXAD profiles of PBAG-based (MW = 2800) PUs and pure PBAG 2800.

ure 11. The data curves, based on the recoverable ratio and temperature, were S-shaped. The recovered temperature  $(T_r)$  of the deformed samples was defined as the inflection point of the curves and the recovered rate  $(V_r)$  was defined as

$$V_r = \frac{dR}{dT} \times \frac{dT}{dt} \tag{15}$$

where R was the recoverable ratio, the  $\frac{dR}{dT}$  was the differential value of the data curve at  $T_r$ , and  $rac{dT}{dt}$  was the average heating rate (~2°C/min).

These data are summarized in Table IV.

The results indicated that the higher the  $T_{\sigma}$  of PUs, the higher the  $T_r$ , as compared with the results of DMA analysis. It indicated that the recovered temperature depended on the glass transition temperature of the soft segment of crosslinked PUs, although there were some differences between these two characteristic temperatures  $(T_g \text{ and } T_r)$  for the different thermal histories of the studied specimens. As in the morphologic analysis studied earlier, the reversible phase was the amorphous PBAG and their glassy state modulus was similar. This result indicates that the ability to fix deformation of the reversible phase was not different from that of others (also



**Figure 7** The DMA analysis of PBAG-based (MW = 1000) PUs.

seen in Figure 11); that is, if the external force was released at a low temperature, the deformation of the sample could be fixed effectively. No recoverable strain of these samples was found until they were heated to the temperature approaching  $T_r$ .

By introducing the chemical crosslinked structure, the strength property was raised at a hightemperature region, and introducing the chemical crosslinked structure also reinforced the amorphous form of PBAG, reinforced effectively in the rubbery state; hence, these deformed samples completely recovered their original shape during the heating process. These results were better than those of linear PUs. On the other hand, the PUs with a higher modulus ratio showed a higher recovered rate than those with a lower modulus ratio. On the basis of DMA analysis, samples with low crosslinked density showed a high modulus ratio. Because the introduction of TMP reinforced the amorphous reversible phase (PBAG), the softening of a hardened reversible phase would be delayed in a high-temperature region; hence, the glassy transition range was broadened and the modulus ratio decreased. This study indicated that the range of recovering deformation is also broadened during the heating process and the value of  $V_r$  is reduced. The samples of PUs with a higher modulus ratio show more excellent shapememory behavior based on the higher recovered rate  $(V_r)$ . Therefore, the less TMP or the longer the length of the soft segment that is used, the better the shape-memory behavior that is observed; the shape-memorized crosslinked estertype PUs render good temperature sensitivity with a high modulus ratio.

The morphology of shape-memory polymers includes fixed phase and reversible phase. Considering the crosslinked ester-type PUs, the fixed phase was the chemical crosslinked point, TMP. The reversible phase was the glassy state of the soft segment, PBAG, with different MW. In this



**Figure 8** The DMA analysis of PBAG-based (MW = 2000) PUs.



**Figure 9** The DMA analysis of PBAG-based (MW = 2800) PUs.

study, the shape-memorized PUs were obtained with different recovered temperatures (-6.8 to 61.3°C) by varying the composition of monomers or the MW of the soft segment; thus, they could be applied at different operating temperatures. They could fix the deformation after cooling to a lower temperature than their  $T_g$ 's under no loading condition and almost recover their original shape after heating the deformed samples. The shapememorized PUs also fixed and recovered from the more complex deformation as shown in Figure 12. Consequently, introduction of a chemical crosslinked structure not only made the deformation recover completely, but also rendered a better shape-memory behavior under the complex deformation.

#### The Comparison of Shape-Memory Behavior Between the Mechanical Viscoelastic Model and Shape-Memorized PUs

Results of the relaxation experiment of five different specimens are shown in Figure 13. It indicates that the tensile stress relaxation modulus E(t, T) approaches an equilibrium value when the time increases. It means that the  $\eta_f(t, T)$  can be thought of as infinity in the crosslinked specimens studies. So, the model can be simplified as shown in Figure 1(b). Equations (1)–(4) can be modified, respectively, as

$$E(t, T) = E_f(T) + E_r(T) \times \exp[-t/\tau_r(T)] \quad (1')$$

$$\sigma(t, T) = \varepsilon_0 \times [E_f(T) + E_r(T) \times \exp[-t/\tau_r(T)]]$$
(2')

$$\varepsilon_f'(t, T) = \varepsilon_0 \tag{3'}$$

$$\varepsilon_f'(t, T) = 0 \tag{4'}$$

On the other hand, the relaxation test under different temperatures (0, 40, and 80°C) was carried out and the parameters of the viscoelastic model, obtained by curve fitting, are summarized in Tables V and VI. The results indicate only a small change of  $E_f$ . Therefore, as mentioned earlier, the  $E_f$  can be thought of as a constant under the range of operating temperature. At low tem-

	Table III	The Storage	• Modulus Rati	io (E' Ratio) <sup>*</sup>	<sup>a</sup> of Crosslinked	Ester-Type PU
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Notation	E' Ratio	Notation	E' Ratio	Notation	E' Ratio
A1	251.1	_	_	_	_
A2	52.1	B2	89.1	C2	112.2
A3	27.1	B3	39.2	C3	48.9
A4	25.0	B4	30.4	C4	35.5
A5	20.7	B5	28.3	C5	31.6
A6	17.4	B6	26.5	C6	28.2

<sup>a</sup> The storage modulus ratio (E' ratio) was defined as  $(E'_{(T_g-20^{\circ}C)}/E'_{(T_g+20^{\circ}C)})$ .



**Figure 10** The DMA analysis of PUs with the same composition (MDI : PBAG : TMP = 4 : 1 : 6/2) but different MW of PBAG.

perature, the model can be simplified as a deformed spring and dashpot in series with the same strain  $\varepsilon_0$ ; hence, eqs. (13) and (14) can be expressed, respectively, as

$$E_f \times \varepsilon + \eta_r(T_2) \times \frac{d\varepsilon}{dt} = 0$$
 (13')

and

$$\frac{d\varepsilon}{dt} = -\frac{E_f \times \varepsilon}{\eta_r(T_2)} \tag{14'}$$

In previous studies of DSC and WAXD, the reversible phase of shape-memorized crosslinked ester-type PUs was in a glassy state; hence, the mechanical properties, which depended on time and temperature, could be based on the Williams–Landers–Ferry (WLF) equation. Consequently, in eqs. (13') and (14'), the value of  $\eta_r(T_2)$ , based on the WLF equation, was very large for the glassy state of the reversible phase at low temperature, as shown in Figure 14.<sup>23</sup> Hence, the value of  $\frac{d\varepsilon}{dt}$  was very small and the strain could not change.



Figure 11 The shape-memory behavior of studied PUs with different MW of PBAG, MW = (a) 1000, (b) 2000, and (c) 2800.

The hardened reversible phase could effectively fix the deformation and resist the elastic recovery of the fixed phase.

Table IV The Shape-Memory Properties: Recovered Temperature  $(T_r)$  and Recovered Rate  $(V_r)$  of the Studied Samples

Samples	$T_r$ (°C)	V <sub>r</sub> (%/min)
A1	8.0	13.82
A2	56.7	11.46
B2	13.4	11.12
B3	39.3	10.74
B4	53.4	10.34
B5	60.7	10.24
B6	61.3	7.40
C2	-6.8	11.54
C3	12.6	10.78
C4	35.1	10.68
C5	47.6	10.42
C6	56.6	9.90



**Figure 12** The shape-memory process of A2 under the complex deformation.

The viscosity of the dashpot of the reversible phase's Maxwell model would reduce during the heating process. According to the WLF equation, it was expressed as

$$\eta_r(T) = \exp\{[-C_1 \times (T - T_g)]/(C_2 + T - T_g)\}$$
  
  $imes \eta_r(T_g)$  (16)

where the universal constant  $C_1 = 40.16$  and  $C_2 = 51.69$ .<sup>24</sup>

If the heating source of the system was linear as  $T = T_2 + at$ , where the constant *a* was heating rate, the differential equation (14') could be expressed as

$$\begin{aligned} \frac{d\varepsilon}{\varepsilon} &= -\frac{E_f}{a \times \eta_r(T_g)} \\ &\times \exp\{[C_1 \times (T - T_g)]/(C_2 + T - T_g)\} \times dT \quad (17) \end{aligned}$$

The initial conduction was  $\varepsilon = \varepsilon_0$  at  $T = T_2$ .

When the factor of fixing deformation disappears, the deformed model recovers for the spring element in the fixed phase's Maxwell model as shown in Figure 1(a-3). Finally, the model recovered its original state as shown in Figure 1(b). Hence, this viscoelastic model describes the mechanism of the shape-memory process quite well.

Combined with eq. (1'), parameters of the model could be obtained from the relaxation test. The results are listed in Table VI. The correlation of strain on temperature  $\varepsilon(T)$  can be obtained from the integration of eq. (17). The reversible



**Figure 13** The relaxation testing curve of the samples: (a) A1, (b) A2, (c) B3, (d) B6, and (e) C6.

ratio of the deformed shape-memorized viscoelastic model is defined as

$$\frac{\varepsilon_0 - \varepsilon(T)}{\varepsilon_0} \times 100\% \tag{18}$$

The viscoelastic model and the corresponding shape-memory behavior of the samples are illustrated in Figure 15.

# Table VThe Relaxation Test at DifferentTemperatures

Sample	Test Temperature (°C)	$E_{f}$ (MPa)	$E_r$ (MPa)
A2	0	163.2	1095
	40	150.7	451
	80	147.7	1.89
C6	0	215.2	753.4
	40	200.7	351
	80	197.5	2.38

Parameter of the Model	Fixed Phase	Reversible Phase			
Sample	Modulus of the Spring (MPa)	Modulus of the Spring (MPa)	Viscosity of the Dashpot $(MPa \ sec^{-1})$	$\tau_r~(\mathrm{sec})$	
A1	102.4	222.6	158.0	0.71	
A2	148.2	219.0	146.7	0.67	
B3	164.0	67.3	210.6	3.13	
B6	198.3	73.5	184.5	2.51	
C6	187.2	61.2	378.2	6.18	

Table VI The Parameters of the Viscoelastic Model of the Studied Samples Based on the Relaxation Test at Their  $T_g$ 

In this study, the modified Maxwell model can describe the shape-memory behavior, fixing and recovering of the deformation, of the crosslinked polymers. When the deformed model was at a low temperature, the viscosity of the dashpot of the reversible phase's Maxwell model was high enough to resist the recoverable elastic force of the fixed phase's Maxwell model. Hence, the recoverable ratio was small at the temperature below the  $T_g$  of the studied specimen. During the heating process, the viscosity  $\eta_r$ , which obeyed the WLF equation, was reduced; the deformation was rapidly recovered on the range of the glass transition of the sample. The recoverable ratio curves of the viscoelastic model were S-shaped as were those of the studied samples; however, the  $T_g$  used in the calculation was monodispersed and was different from the polydispersed  $T_g$  of the studied samples. Hence, the change of the recov-



**Figure 14** The WLF equation for  $\eta_r(T)$ .<sup>23</sup>

erable ratio of the viscoelastic model was sharper than that of crosslinked ester-type PUs. On the other hand, the sample with the high modulus ratio and recovered rate showed the better-fitting result than that with the low modulus ratio and recovered rate.

## CONCLUSION

The morphology of shape-memorized crosslinked ester-type polyurethanes was studied by DSC, WAXD, and DMA. The results indicated that the fixed phase was the chemical crosslinked point, TMP, and the reversible phase was the amorphous state of PBAG with the different MW. When the higher content of TMP was introduced: (1) the higher  $T_g$ ; (2) the broader range of glass transition; and (3) the lower modulus ratio of studied samples were found. When the longer length of the reversible phase (PBAG) was used: (1) the lower  $T_g$  and (2) the higher modulus ratio of PUs were obtained. After comparing these results with the shape-memory behavior testing, the shape-memory behavior was found to be dependent on the morphology of samples; that is, the deformed PUs with a high  $T_g$  showed a high recoverable temperature, and those with a high modulus ratio showed a high recoverable rate. On the other hand, the shape-memorized viscoelastic model, consisting of two Maxwell models connected in parallel, was proposed. This model explains how the reversible phase can fix the deformation without external force and how the fixed phase can memorize the original shape and recover it.



**Figure 15** The comparison of the shape-memory behavior between the viscoelastic model (solid line) and the tensile experiment data of (a) A1, (b) A2, (c) B3, (d) B6, and (e) C6.

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