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The Mechanical-Viscoelastic Model and WLF Relationship in Shape Memorized Linear Ether-Type Polyurethanes

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Abstract: A modified mechanical-viscoelastic model with two Maxwell models in parallel is proposed to describe the shape memory behavior of segmented polyurethanes (PUs). Based on the view of viscoelasticity, the influence of the fixed phase (hard segment) and the reversible phase (soft segment) on the shape memory effect is studied. The WLF equation is adopted to describe the relationship between the viscosity of the reversible phase and the temperature by using the selected reference temperature and the adjustable parameters. The parameters of the WLF equation are dependent on the M.W. of the soft segment of PUs. Finally, the model could properly describe the mechanism of shape memory behavior of segmented PUs. Moreover, the change of the recoverable curve of the deformed model is similar to that of experimental datapoints.

Keywords: Segmented polyurethanes, Shape memory behavior, Maxwell model, Relaxation, WLF equation.

Introduction

If polymers show shape memory behavior, their morphology should contain two phases [1,2]. One phase is the fixed phase, where no phase transition is found at the operating temperature range. At this phase one can recover the deformation after heating to a high temperature, which is below its characteristic temperature (T_H). The fixed phase is glassy, with a high glass transition temperature (T_g). It is also crystal, with a high crystal melting temperature (T_m) exhibited as the physical crosslinked point or the chemical crosslinked point. The other phase is the reversible phase, which is found following phase transition as a series of thermal processes (heating or cooling).

$$\text{Glassy state} \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} \text{rubbery state,}$$

$$\text{or} \quad \text{crystal} \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} \text{crystal melting}$$

Hence, the polymer can be hardened to resist the recoverable force from the fixed phase under low temperature. However, the change in strength of the reversible phase is great during the heating process, and the fixed deformation can be recovered easily and effectively. Consequently, it is glassy with low T_g or crystal with low T_m. For this cause, the viscoelastic properties of these two phases are necessary for deciding whether the deformation could be effectively fixed for a long time under no external force loading. They can also determine whether the deformed materials could recover their original shape memory or not.

In the literature [3-13] and in our previous study [14,15], it was shown that the morphology could strongly influence the shape memory behavior of polymers. Takahasli et al. and Hayashi have studied the thermal structure and dynamic mechanical properties of two series of segmented PUs with the shape memory behavior [3,6-9]. Hirai et al. has studied the influence of chemical crosslinked structures on the shape memory behavior of poly(vinyl alcohol) hydrogel [4,5]. Kim et al. and Li et al. studied the effect of crystallization of polycaprolacton (PCL), in the reversible phase, on the shape memory behavior of PUs [10-12]. Li introduced the

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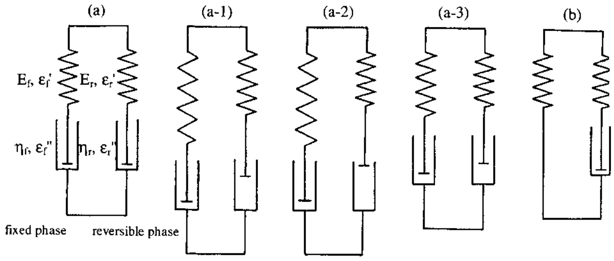

Figure 1. The viscoelastic model and mechanism of the shape memory polymer; (a) the general model of the shape memory polymer; (b) the simplified model of the crosslinked shape memory polymer; (a-1) deformed to ε_0 at T_1; (a-2) kept the strain ε_0 at T_1 for a long time, then cooled to T_2 and released the force; (a-3) heated at the rate of $T = T_2 + at$, and the model recovered to its original state after heating.

structure of interpenetrating polymer networks (IPN) to shape memorized polyacrylamide [13]. However, there are few reports, which study the relationship between the viscoelastic properties of these two phases and the shape memory behavior of polymers. In our study [14,15] for these shape memorized linear polyether-type PUs, the fixed phase was the hard segment (MDI+BD). And the reversible phase was the soft segment that was amorphous PTMO with different molecular lengths and mixed with short hard segments. Moreover, a modified Maxwell model was proposed to describe the shape memory behavior of the polymer [16]. For studying the relationship between the viscoelastic properties of these two phases and the shape memory behavior of PUs, a tensile relaxation test was performed to obtain the viscoelastic parameters of these specimens.

Mechanical-viscoelastic model

The viscoelastic properties of polymers can not be properly described by the spring or the dashpot individually. Therefore, the Maxwell model and the Voigt model were proposed to describe the mechanical behavior of polymers. Additionally, several generalized models were proposed to explain the mechanical response of polymers with two transitions. One was the Maxwell-Wiechert model [17], a generalized Maxwell model that consisted of an arbitrary number of Maxwell models connected in parallel. The other was the Voigt-Kelvin model [17], a generalized Voigt model that consisted of an arbitrary number of Voigt models connected in series. As mentioned above, the morphology of the shape memory polymers is composed of fixed phases and reversible phases. The difference in their characteristic temperatures is quite large. That is, the phase transition of the reversible phase occurs at a low temperature (T_L), but that of the fixed phase occurs at a high temperature (T_H). Based on segmented PUs, Bonart [18] proposed a mechanical model based on the Maxwell-Wiechert model to characterize the segment mobility and the crosslinking stability of the thermoplastic elastomer. Consequently, for shape memorized polymers, a viscoelastic model consisted of two Maxwell models connected in parallel was proposed [16]. These two Maxwell models represent the reversible phase and fixed phase individually as shown in Figure 1(a). The mechanical behavior and the mechanism of the shape memory behavior of the mechanical-viscoelastic model were described as follows:

(1) At a high temperature (ex. $T_L<T_1 = 80$ °C $< T_H$), the model was stretched to a constant strain ε_0 and maintained this constant strain, shown in Figure 1(a-1). The modulus (E) and stress (σ) of the model are the function of time and temperature, obtained from the relaxation test, expressed as follows [17]:

$$E(t, T) = E_f(T) \cdot e^{-t/\tau_f(T)} + E_r(T) \cdot e^{-t/\tau_r(T)} \quad (1)$$

$$\sigma(t, T) = \varepsilon_0 \cdot [E_f(T) \cdot e^{-t/\tau_f(T)} + E_r(T) \cdot e^{-t/\tau_r(T)}] \quad (2)$$

The subscript of "f" and "r" denote the fixed phase and reversible phase individually, and "E" denotes the modulus of spring within the Maxwell model. The relaxation time "τ" is defined as

$$\tau_i = \frac{\eta_i}{E_i} \quad (3)$$

where the subscript "i" denotes "f" or "r", and "η" denotes the viscosity of dashpot within the Maxwell model. Hence, the strains of the elements in the viscoelastic model are obtained [17]

$$\varepsilon_i'(t, T) = \varepsilon_0 \cdot e^{-t/\tau_i(T)} \quad (4)$$

$$\varepsilon_i''(t, T) = \varepsilon_0 \cdot (1 - e^{-t/\tau_i(T)}) \quad (5)$$

where ε' and ε'' are the strains of spring and dashpot, respectively. The parameters (E_f, E_r, τ_f, τ_r, η_f, η_r) of the viscoelastic model can be obtained from the E-t curves of the relaxation test as shown in Figures 2~4.

(2) At a high temperature ($T_1 = 80$ °C), the value of the modulus and viscosity of the reversible phase used in the Maxwell model are low. Hence, when the strain is kept at a high temperature (e.g. $T_1 = 80$ °C) for a long time (t_∞), the value of ε_r'' approaches ε_0. The value of ε_r' shifts to zero. But the same strain (ε_0) in the fixed phase

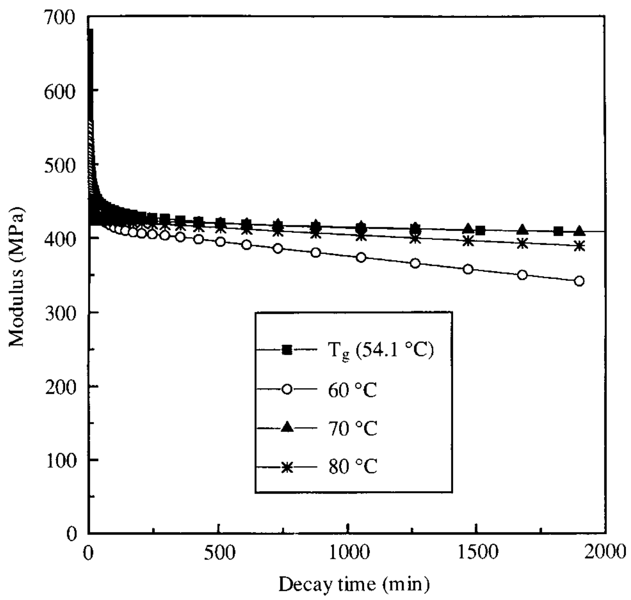

Figure 2. The relaxation testing curve of L1.

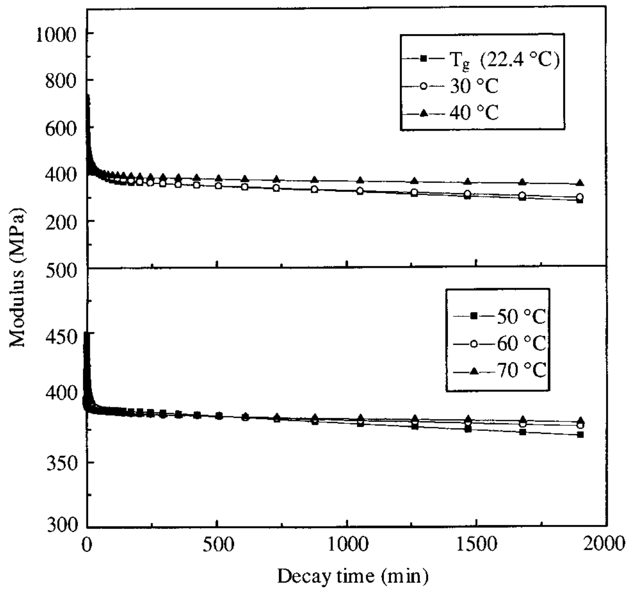

Figure 3. The relaxation testing curve of L2.

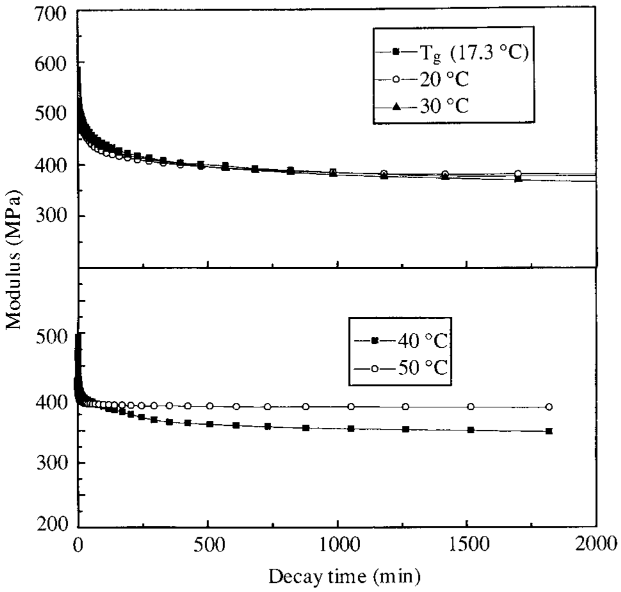

Figure 4. The relaxation testing curve of L3.

Maxwell model is contributed by ε_f' and ε_f'' as shown in Figure 1(a-2). The relationship between these strains is expressed as

$$\varepsilon_0 = \varepsilon_f' + \varepsilon_f'' = \varepsilon_r'' \tag{6}$$

Then, this system is maintained at that constant strain and cooled to a low temperature (ex. $T_2 = -20$ °C $< T_L$). The model can be simplified as a deformed spring and dashpot in series, then combined with a deformed dashpot in parallel. The operating temperature is far from the characteristic temperature of the fixed phase. Therefore, the values of E_f and η_f can be thought of as constant under the temperature range of operation.

(3) Under the condition of no external force loading, the viscid fluid (dashpot) could not render a mechanical response. Hence, the strain of the dashpot of the fixed phase Maxwell model (ε_f'') will not change any more, and it can be obtained from Eq.(5).

$$\begin{aligned}\varepsilon_f''(t_\infty, T_1) &= \varepsilon_0 \cdot (1 - e^{-t_\infty/\tau_f(T_1)}) \\ &= \varepsilon_f''\ (t'(=0), T_2) \end{aligned} \tag{7}$$

The other strain of elements in the mechanical-viscoelastic model can also be obtained:

$$\varepsilon_f'(t_\infty, T_1) = \varepsilon_0 \cdot e^{-t_\infty/\tau_f(T_1)} \tag{8}$$

$$\varepsilon_r''(t_\infty, T_1) = \varepsilon_0 \tag{9}$$

On the other hand, the total stress is zero. Therefore,

$$\sigma_f + \sigma_r = 0 \tag{10}$$

where σ_f indicates the recoverable stress of the deformed spring of the fixed phase Maxwell model. σ_r is the resisted stress of the deformed dashpot in reversible phase. Using the Hook's law and Newton's' law, Eq.(10) is shown as follows:

$$E_f \cdot \varepsilon_f' + \eta_r(T_2) \cdot \frac{d\varepsilon_r''}{dt} = 0 \tag{11}$$

Equation (11) is rearranged and the strain rate, $\frac{d\varepsilon_r''}{dt}$,

Table I. The composition of samples [15].

Notation	MDI: PTMO: BD	M.W. of PTMO
L1	12/1/11	250
L2	12/1/11[(a)]	1000
L3	12/1/11	2000

(a) It indicates the molar ratio of monomers.

Table II. The properties of samples [15].

Notation	T_g (°C)[(a)]	Modulus ratio	T_r (°C)	V_r (%/min)
L1	54.1	3.87	61.3	6.4
L2	22.4	4.01	42.5	5.4
L3	17.3	4.05	26.2	5.38

(a) T_g was measured by DMA.

Table III. The results of the relaxation testing.

Temperature (°C)	E_f (MPa)	E_r (MPa)	η_r (MPa • sec)
L1			
T_g (54.1)	430.5	206.3	6.82×10^4
60	428.8	104.4	2.17×10^4
70	428.0	21.3	3.72×10^3
80	425.0	5.2	5.40×10^2
L2			
T_g (22.4)	404.4	278.9	7.75×10^4
30	397.1	132.6	3.86×10^4
40	402.6	98.5	3.23×10^4
50	393.2	48.3	1.07×10^4
60	391.4	25.4	5.18×10^3
70	389.3	10.2	2.55×10^3
L3			
T_g (17.3)	395.3	151.7	5.25×10^4
20	397.4	121.4	3.45×10^4
30	389.4	110.4	2.17×10^4
40	391.2	86.1	1.25×10^4
50	391.7	33.1	4.91×10^3

is obtained

$$\frac{d\varepsilon_r''}{dt} = -\frac{E_f \cdot \varepsilon_f'}{\eta_r(T_2)} \qquad (12)$$

Equation (12) could be used to discover whether the deformation of a shape memorized viscoelastic model could be fixed or not. That is, if the viscosity $\eta_r(T_2)$ was large, the strain rate would be reduced to a small value, even to zero. And, 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.

(4) The viscosity of dashpot of the reversible phase Maxwell model is reduced during the heating process. When the factor of fixing deformation disappears, the deformed model will recover by the elastic force of the spring element in the fixed phase Maxwell model as showing in Figure 1(a-3). Finally, the model recovers to the original state, as shown in Figure 1(a). Hence, this viscoelastic model could describe the mechanism of the shape memory process quite well.

Experimental

1. Materials

Reagent-grade poly(tetramethylene oxide) glycol (PTMO, M.W. = 2000, 1000 and 250, Aldrich Chemical Co.) and 1,4-butane diol (BD, Aldrich Chemical Co.) were dehydrated under a vacuum at 65 °C before using. Reagent-grade 4,4'-diphenyl methane diisocyanate (MDI, Tokyo Chemical Inc.) was melted at 45 °C and used after removing the white precipitates in the melts. Reagent-grade *N*,*N*'-dimethyl foramide (DMF, Aldrich Chemical Co.) was dehydrated with molecular sieves (4 Å) and used as a solvent.

2. Polymer synthesis

Three PUs of varying soft segment length were synthesized with MDI, PTMO, and BD as the chain extender. The compositions of the materials are listed in Table I. A modified two-step polymerization was adopted. The dehydrated MDI and PTMO were mixed at the mole ratio (12/1) at 45 °C and reacted at 65 °C for 3 hours. For the second step, the NCO-capped prepolymer was diluted with the DMF, and the dilute solution of BD in DMF was added slowly at 0 °C. After mixing completely, the reaction system was heated to 65 °C for 4 hours. The reaction took place under a nitrogen gas atmosphere in order to avoid the influence of the moisture during the synthesis process. The PU solution was casted on the glass plate and kept at 65 °C for 24 hours. Finally, the PU film was immersed in purified water overnight. Then, the DMF was removed under a vacuum at 65 °C for 24 hours.

3. Polymer characterization

3.1 Relaxation test

A DuPont 983 DMA, in the relaxation mode, was used to carry out the relaxation test under a constant strain of 5%. The test temperatures are listed in Table III.

3.2 Shape memory behavior

The shape memory behavior was examined by a tensile test as follows. The specimen was deformed to a constant strain (ε_0 = 50%) at 80 °C and kept at deformation for 300 min. The deformed specimen was quenched to -20 °C for 2 min, then the external force was released. Finally, the deformed sample was heated at a fixed heating rate (2 °C/min) and the relationship between the recoverable ratio and the temperature was reported. The ratio of the recovery was defined as $(\varepsilon_0 - \varepsilon(T))/\varepsilon_0 \times 100\%$. 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

$$V_r = \frac{dR}{dT} \cdot \frac{dT}{dt} \tag{13}$$

where R was the recoverable ratio, the $\frac{dR}{dT}$ was the differential value at T_r, and $\frac{dT}{dt}$ was the average heating rate (≈2 °C/min). The properties of the specimens are listed in Table II [14,15].

Results and Discussion

The relaxation test under different temperatures was carried out and is shown in Figure 2~4. The parameters of the viscoelastic model were obtained by fitting the data to Eq.(1), and they are summarized in Table III. The results indicate that E_r changes very little. Therefore, as mentioned above, the E_f could be thought of as a constant under the range of operating temperature. Since, the curve of relaxation decays slowly for a long time, the value of η_f is large and the change of ε_f'' is very small and can be ignored. Consequently, the mechanical-viscoelastic model can be simplified, as shown in Figure 1(b). On the other hand, the value of η_r is low at high temperatures, so, the strain of the reversible phase model is almost contributed by the dashpot after a long time. And the spring strain of the reversible phase model would be reduced to zero. Hence, Eqs.(11) and (12) could be expressed as

$$E_f \cdot \varepsilon + \eta_r(T_2) \cdot \frac{d\varepsilon}{dt} = 0 \tag{11-1}$$

and

$$\frac{d\varepsilon}{dt} = -\frac{E_f \cdot \varepsilon}{\eta_r(T_2)} \tag{12-1}$$

The study to express the effect of free volume on viscosity, Doolittle equation [17], has led to the derivation of relationships commonly known as WLF type equations. Ferry et al. have used them to explain the flow behavior of polymer melts [19]. One form of WLF equation is given as follows:

$$\ln \frac{\eta}{\eta_{T_g}} = \frac{-A \cdot (T - T_g)}{B + T - T_g} \tag{14}$$

Table IV. Details of the WLF equation fit to experimental data.

Notation	T_0 (°C)$^{(a)}$	A	B
L1	54.1	20	100
L2	22.4	15	150
L3	17.3	10	150

(a) The reference temperature (T_0) is T_g of the sample.

where A and B are constants. Consequently, in Eqs. (11-1) and (12-1), the value of $\eta_r(T_2)$ is based on the WLF equation. The value of $\frac{d\varepsilon}{dt}$ is very small and the strain can not change at low temperatures. The hardened reversible phase can effectively fix the deformation and resist the elastic recovery of the fixed phase. The viscosity of dashpot of the reversible phase Maxwell model lowers during the heating process, according to WLF equation, is expressed as

$$\eta_r(T) = e^{\left(\frac{-A \cdot (T - T_g)}{B + T - T_g}\right)} \cdot \eta_r(T_g) \tag{15}$$

If the heating source of the system is linear as ($T = T_2 + at$) where the constant "a" is heating rate, the differential Eq.(12-1) can be expressed as i.e.,

$$\frac{d\varepsilon}{\varepsilon} = -\frac{E_f}{a \cdot \eta_r(T_g)} \cdot e^{\left(\frac{A \cdot (T - T_g)}{B + T - T_g}\right)} \cdot dT$$

$$\varepsilon = \varepsilon_0 \text{ at } T = T_2 \tag{16}$$

Originally, A and B were thought to be universal constants (A = 17.44 and B = 51.6), but the same authors [19] and others researchers [20-22] have shown that A and B are material specific. Wicks et al. [23] used the WLF equation by treating the universal constants as adjustable parameters. Hartmann and Lee [24] showed that A and B would increase with increasing the length of the soft segment (poly propylene glycol). The chemical structure (interpenetrating polymer networks) would influence the constants of the WLF equation by the study of Akay et al. [25]. For our studied specimens, the constants, A and B, were obtained. And they are listed in Table IV. Finally, the recoverable curves of the deformed model were derived. And the results are shown on the Figure 5. The comparison between the experimental datapoints and the models' curves were studied. The results are found that the mechanical viscoelastic model can properly describe the shape memory behavior of polymers. That is to say, it can fix the deformation at low temperatures and recover to the original shape during heating process. However, there are some dis-

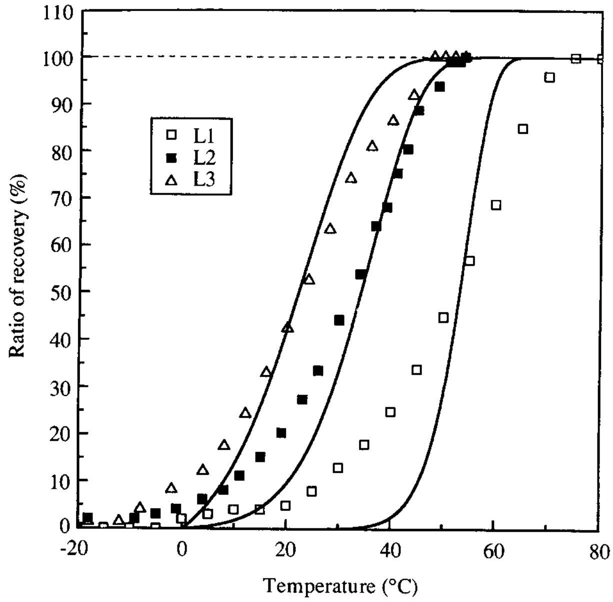

Figure 5. The shape memory behavior of specimens. Solid lines indicate the recoverable ratio curve of the model.

crepancies between the model's curves and the experimental datapoints. The viscoelastic properties of the reversible phase (soft segment) are independent on those of the fixed phase (hard segment). Moreover, the T_g used in calculation is mono-dispersed and it is different from the poly-dispersed T_g of our studied specimens. Hence, all of the factors that could influence the shape memory behavior of PUs and their effects should be studied in the future.

Conclusions

In our previous study, a shape memorized viscoelastic model consisting of two Maxwell models connected in parallel was proposed. These two Maxwell models represented individually reversible phase and fixed phase for their different characteristic temperatures. This model could describe the detailed process of the shape memory mechanism of crosslinked ester-type PUs [16] and the influence of the reversible phase and the fixed phase on shape memory behavior. In this study, the mechanical-viscoelastic model also characterized the shape memory behavior of linear segmented PUs. That is, how the reversible phase (soft segment) fixed the deformation without external force. And how the fixed phase (hard segment) memorized the original shape and recovered it. Based on the WLF equation with selected temperature and the adjustable parameters, the recoverable curve of the deformed mechanical-viscoelastic model showed changed similar to those of experimental datapoints.

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