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Shape recovery and irrecoverable strain control in polyurethane shape-memory polymer

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Abstract

In shape-memory polymers, large strain can be fixed at a low temperature and thereafter recovered at a high temperature. If the shape-memory polymer is held at a high temperature for a long time, the irrecoverable strain can attain a new intermediate shape between the shape under the maximum stress and the primary shape. Irrecoverable strain control can be applied to the fabrication of a shape-memory polymer element with a complex shape in a simple method. In the present study, the influence of the strain-holding conditions on the shape recovery and the irrecoverable strain control in polyurethane shape-memory polymer is investigated by tension test of a film and three-point bending test of a sheet. The higher the shape-holding temperature and the longer the shape-holding time, the higher the irrecoverable strain rate. The equation that expresses the characteristics of the irrecoverable strain control is formulated.

Keywords: shape-memory polymer, shape recovery, shape fixity, irrecoverable strain, polyurethane, strain-holding condition

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

In shape-memory materials that are used as intelligent materials, the amount of recovery deformation is particularly large in shape-memory polymer (SMP) and its practical application is widely expected [1, 2]. Since the properties of molecular motion differ above and below the glass transition temperature T_g, the shape that is deformed above T_g is fixed below T_g and the original shape is recovered from the fixed shape by heating. Such shape fixity and shape recovery can be used in practical applications. The polyurethane-series (PU) SMP can be used in molding, potting, casting, microbeads and foam types. The PU–SMP can be molded by such methods as injection, extrusion and blowing, similar to conventional plastics [3, 4]. It can be made any color as it is transparent. The T_g can be set in the region of room temperature ± 50 K. The range of the glass transition region is narrow. The difference in the elastic modulus above and below T_g is large. The moisture permeability of the film varies significantly above and below T_g, and the volume change of foam is large. The PU–SMP, therefore, has been practically applied over a wide range of fields, for example, as an autochoke element for engines, an intravenous cannula in the medical field, and knife and fork handles for handicapped persons. In the case of SMP foam, applications are expected in the aerospace field, since the foam is light and a large variation in volume can be achieved. In this case, it is particularly important for the SMP foam elements to hold the fixed shape for a long time and to regain their original shape thereafter [5]. It was confirmed that both the rates of shape fixity and shape recovery are close to 100% if the deformed shape is held at temperatures below T_g.

It was confirmed, in the research on the long-term characteristics of SMP foam, that shape fixity and shape recovery become imperfect and irrecoverable strain appears depending on the strain-holding conditions of temperature, time and strain. From the viewpoint of fabricating SMP elements, if we can control the irrecoverable strain properly, we can obtain a new intermediate shape between the fixed shape and the original shape. In order to fabricate complex SMP elements, we require a complex metal mold. Such a metal mold is difficult to produce and expensive. For example, a flat SMP sheet is easy to produce in the first process and we can easily obtain the desired shape different from the flat sheet in the following process. This technique has been used in practice to obtain a new shape different from the primary one, and we have named the technique secondary-shape forming [6]. The irrecoverable strain appears depending on the strain-holding conditions [7]. From the viewpoint of the evaluation of the thermomechanical properties of SMPs, the influence of the strain-holding conditions on shape recovery and irrecoverable strain is important. If the irrecoverable strain is applied to fabrication of the SMP elements, elements with complex shapes can be fabricated by a simple method without the need of a metal mold. That is, a useful fabrication method can be newly developed for the SMP elements by making use of the irrecoverable strain.

In the present study, the basic properties of shape recovery and irrecoverable strain control were investigated by the tension test of a PU–SMP film. In many cases of practical applications, the SMP elements are subjected to bending, and therefore, the properties are also investigated by three-point bending test of a SMP sheet. In the tests, the influence of the strain-holding conditions on the shape recovery and the irrecoverable strain is examined. The main factors that affect these characteristics are the strain-holding temperature, holding time and holding strain. On the basis of the results obtained from the experiment, it is found that irrecoverable strain is slight at holding temperatures below T_g and increases with increasing holding temperature and holding time at holding temperatures above T_g. An equation that expresses the irrecoverable strain control is formulated on the basis of the experimental results.

2. Experimental method

2.1. Materials and specimen

2.1.1 SMP film. The material used in the tension test was a PU–SMP film (Diary MM6520, produced by Mitsubishi Heavy Industries, Ltd). The thickness of the film was 0.25 mm. The width and the length of the testing part were 10 and 40 mm, respectively. To hold the specimen property without slippage, the width and length of the gripping parts of both ends of the specimen were 42 and 33 mm, respectively. The glass transition temperature T_g was defined as that at the midpoint of the glass transition region in which the storage elastic modulus E' changes. The T_g was obtained by dynamic mechanical test with the frequency of 1.0 Hz at 338 K. The main glass transition region of PU–SMP exists between $T_g - 15$ K and $T_g + 15$ K [8].

2.1.2 SMP sheet. The material used in the bending test was a PU–SMP sheet (Diary MP9000, produced by Mitsubishi Heavy Industries, Ltd). The thickness, length and width of the specimen were 5.0, 60 and 10 mm, respectively. The distance between two supports was 40 mm in the three-point bending test. The T_g obtained by dynamic mechanical test was 373 K.

2.2. Experimental apparatus

The thermomechanical load with loading–unloading and heating–cooling was applied using a shape-memory-material testing machine [9]. The testing machine was composed of a tensile machine, for loading and unloading, and a temperature-controlling device for heating and cooling. The load was measured using a load cell. The displacement of the gauge length in the tension test and the deflection of the midpoint in the bending test were measured from the displacement of a crosshead. The temperature was measured using a thermocouple with a diameter of 0.1 mm, which was set close to the surface on the central part of the specimen in tension test (1) and set close to the end of the pushing rod that presses the central part of the specimen in bending test (2). Hot and cold air flows were controlled so as not to flow directly to the specimen.

In the test of holding the bent form of the sheet for a long time, a shape-fixing jig was used to hold the bent form after inducing the prescribed deflection. The shape-fixed specimen was held at the prescribed temperature in a furnace.

2.3. Experimental procedure

2.3.1 Tension test of film. The characteristics of shape recovery and irrecoverable strain control of the SMP film were investigated by the tension test. In the test, load was applied under a strain rate of 20% min^{-1}, and the maximum strains were 30 and 50%. The tension test was carried out by the following procedure:

i. Maximum strain ε_{max} was applied at $T_g + 20$ K.
ii. Holding ε_{max} constant, the specimen was cooled to room temperature. The strain was fixed at this stage and was held thereafter. Therefore, the holding strain ε_h is equal to ε_{max}.
iii. After cooling, the specimen was heated to the prescribed holding temperature T_h(T_g, $T_g + 10$ K and $T_g + 20$ K) by holding ε_h constant.
iv. Strain ε_h was held at T_h for the prescribed holding time t_h (0.5, 1, 2, 3, 4 and 8 h).
v. Load was removed after holding ε_h for t_h.
vi. The specimen was heated to $T_g + 30$ K under a no load condition. Note that strain is recovered in this stage.

2.3.2 Bending test of sheet. The characteristics of shape recovery and irrecoverable strain control of the SMP sheet were investigated by the following two kinds of three-point bending tests: (i) bending test with a short holding time, and(ii) bending test with a long holding time. In both tests, deflection rate dy/dt was $2\,mm\,min^{-1}$ and maximum deflection y_{max} was 15 mm.

(i) Bending test with a short holding time

i. The maximum deflection y_{max} was applied at $T_g + 20\,K$ under the deflection rate dy/dt of $2\,mm\,min^{-1}$.

ii. Holding y_{max} constant, the specimen was cooled to room temperature. The deflection was fixed at this stage and was held thereafter. Therefore, the holding deflection y_h is equal to y_{max}.

iii. After cooling, the specimen with y_h was heated to the prescribed holding temperature $T_h (T_g, T_g + 10\,K, T_g + 20\,K$ and $T_g + 30\,K)$.

iv. The deflection y_h was held at T_h for the prescribed holding time t_h (0.5, 1, 2, 4 and 8 h).

v. The pushing rod was lifted after holding ε_h for t_h.

vi. The specimen was heated to $T_g + 20\,K$ under a no-load condition.

(ii) Bending test with long holding time

Experimental stages *i* and *ii* were the same as those in the bending test with short holding time (i).

iii. After cooling, the specimen with y_h was inserted into the holding jig and then held in a furnace at the prescribed holding temperature $T_h (T_g, T_g + 10\,K, T_g + 20\,K$ and $T_g + 30\,K)$.

iv. The deflection y_h was held at T_h for the prescribed holding time t_h (18, 24, 48, 72 and 96 h).

v. The specimen was unloaded by removing the holding jig after holding y_h for t_h.

vi. The specimen was heated to $T_g + 20\,K$ under a no-load condition.

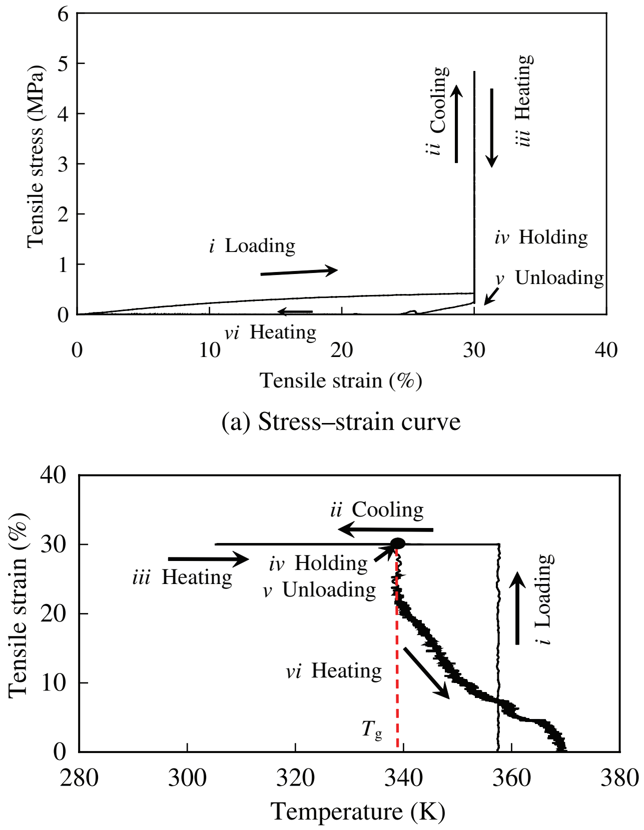
3. Experimental results and discussion

In dealing with the experimental data, stress and strain were treated in terms of nominal stress and nominal strain, respectively. Tensile strain was calculated for the initial gauge length of 40 mm even in the recovery process. The numerals *i–vi* used in the figures showing the experimental results correspond to the loading processes explained in the experimental procedure.

3.1. Shape recovery and irrecoverable strain control in tension

3.1.1 Stress–strain–temperature relationship

a. Deformation behavior in the case of unloading without holding time The stress–strain curve and strain–temperature curve obtained by the tension test of the film for the holding strain $\varepsilon_h = 30\%$, the holding temperature $T_h = T_g$ and the holding time $t_h = 0$ are shown in figures 1(a) and (b), respectively. In the figure, some fluctuations of the curves appear due to the experimental conditions of control. As can be seen in figure 1(a), the recovery stress $\sigma_r = 5\,MPa$ appears in cooling process *ii* to room temperature when ε_h is held constant. The recovery stress is induced by thermal stress resulting from strain holding



(a) Stress–strain curve

(b) Strain–temperature curve

Figure 1. Stress–strain curve and strain–temperature curve for $\varepsilon_h = 30\%$, $T_h = T_g$ and $t_h = 0$ for SMP film subjected to tension.

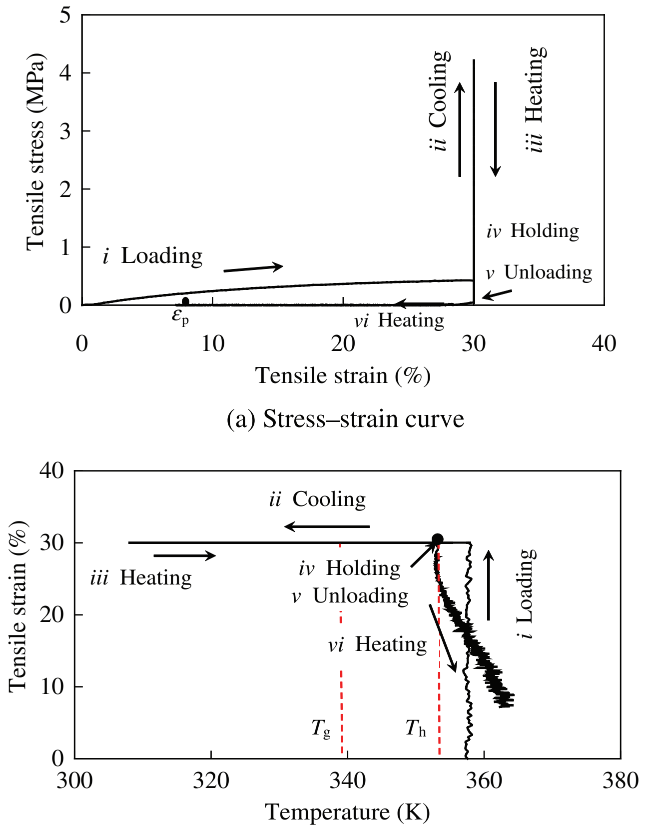
against thermal contraction in the cooling process [8]. In heating process *iii* and holding process *iv* ($t_h = 0$ in this case), stress decreases. Strain is recovered by 4% in unloading process *v*, and is recovered in heating process *vi*.

As can be seen in figure 1(b), strain is recovered gradually with increasing temperature in heating process *vi* under no load, and it is recovered completely by heating to $T_g + 30\,K$. Strain recovery occurs owing to the micro-Brownian motion of soft segments of SMP, which is activated if the material is heated to temperatures above T_g.

b. Deformation behavior in the case of holding at high temperature for a certain time. The stress–strain curve and strain–temperature curve obtained by the tension test for the holding strain $\varepsilon_h = 30\%$, the holding temperature $T_h = T_g + 15\,K$ and the holding time $t_h = 2\,h$ are shown in figures 2(a) and (b), respectively.

As can be seen in figure 2(a), though the overall stress–strain curve is similar to that shown in figure 1(a), stress decreases to a nominal amount in heating process *iii* and in holding process *iv* under constant strain ε_h.

As can be seen in figure 2(b), although strain recovers gradually with increasing temperature in heating process *vi* under no load, strain ε_p of 7%, which corresponds to 23% of ε_h, is not recovered by heating to $T_g + 30\,K$. If the SMP is held at temperatures above T_g, reorientation of the molecular



(a) Stress–strain curve

(b) Strain–temperature curve

Figure 2. Stress–strain curve and strain–temperature curve for $\varepsilon_h = 30\%$, $T_h = T_g + 15$ K and $t_h = 2$ h for SMP film subjected to tension.

chain proceeds because of the thermal motion of molecular chains (micro-Brownian motion) and therefore, the original shape is not recovered completely, resulting in the appearance of irrecoverable strain.

3.1.2 Characteristics of irrecoverable strain control. In the present study, from the viewpoint of the practical use of shape recovery and irrecoverable strain control, the residual strain that appears by heating to $T_g + 30$ K after strain holding is defined as irrecoverable strain, and the characteristics of irrecoverable strain control are evaluated.

The influence of the strain-holding conditions of holding time t_h, holding temperature T_h and holding strain ε_h on irrecoverable strain was investigated in the experiment. In order to evaluate irrecoverable strain control using irrecoverable strain ε_p obtained from the experiment, the irrecoverable strain rate S is defined as

$$S = \frac{\varepsilon_p}{\varepsilon_h}, \qquad (1)$$

where S denotes the ratio of irrecoverable strain ε_p to holding strain ε_h. The relationships between S and the holding time t_h obtained from the experiment are shown by various symbols in figure 3. As can be seen, the higher the holding temperature T_h, the higher the S. S increases with increasing t_h and gradually saturates to a certain value with decreasing an inclination.

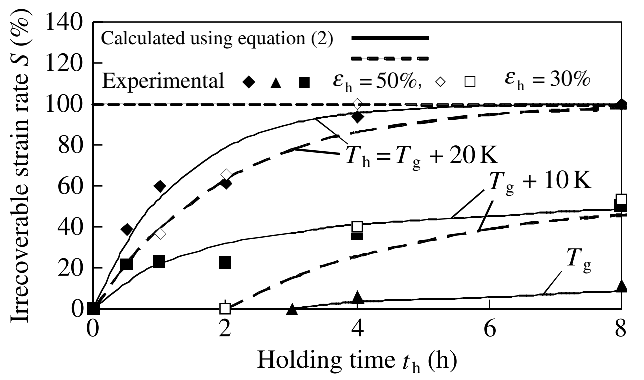


Figure 3. Relationship between irrecoverable strain rate S and holding time t_h at $T_h = T_g$, $T_g + 10$ K and $T_g + 20$ K for SMP film subjected to tension: Experimental results and results approximated using equation (2).

An equation for evaluating irrecoverable strain rate S is necessary if the irrecoverable strain control is applied to the fabrication of SMP elements. On the basis of the characteristics of S shown in figure 3, the dependence of S on t_h can be expressed as

$$S = S_p\left(1 - e^{-(t_h - t_s/c)}\right), \qquad (2)$$

where S_p, t_s and c denote the saturated value of S, the critical time before irrecoverable strain appears, and the time constant, respectively. The results calculated with equation (2) using parameter values such that the characteristics of S obtained from the experiment are approximated are shown by the solid and broken lines in figure 3. As can be seen, the characteristics of S can be expressed well by equation (2). As can be seen from the behavior of S shown in figure 3, if T_h is high, irrecoverable strain appears in a short holding time for each holding strain ε_h, and the irrecoverable strain rate S is large. If T_h is low and close to T_g, a long holding time is needed for irrecoverable strain to appear, and S is small. The larger the holding strain ε_h, the earlier the appearance of irrecoverable strain.

These characteristic values, S_p, t_s and c, depend on the holding temperature T_h. The characteristic values to approximate the experimental results can be expressed by the function of the holding temperature T_h as follows:

$$\left.\begin{aligned} S_p &= 0.04(T_h - T_g) + 0.12 \\ c &= -0.26(T_h - T_g) + 6.6 \\ t_s &= -0.16(T_h - T_g) + 2.7 \end{aligned}\right\}. \qquad (3)$$

The results calculated using equations (2) and (3) are shown by the solids lines in figure 4. As can be seen, the characteristics of S can be expressed well by equations (2) and (3).

The tensile properties of the SMP film, as discussed above, reveal that irrecoverable strain ε_p is proportional to ε_h if the material is held at temperatures above T_g. Irrecoverable strain rate can be expressed as functions of t_h and T_h. These equations of the characteristics of S are useful when irrecoverable strain control is applied in the fabrication of the SMP elements.

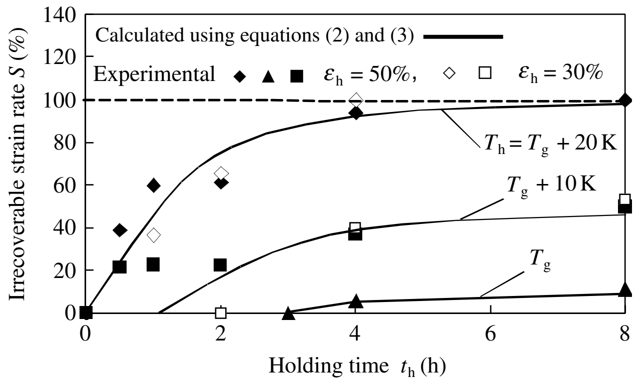


Figure 4. Relationship between irrecoverable strain rate S and holding time t_h for SMP film subjected to tension, calculated using equations (2) and (3).

3.2. Shape recovery and irrecoverable strain control in bending

3.2.1 Deformed states in bending. Photographs of the various states of the SMP sheet in the three-point bending test for $T_h = T_g$ and $t_h = 4$ h are shown in figure 5 for the initial state (a), the deformed state at the maximum deflection $y_{max} = 15$ mm (b), the shape-fixed state after cooling to room temperature (c) and the recovered state after heating to $T_g + 20$ K (d). The deformed state at a temperature above T_g in figure 5 (b) is fixed by cooling to below T_g, as can be seen in figure 5(c). If the sheet is heated to $T_g + 20$ K after holding the maximum deflection at $T_h = T_g$ for $t_h = 4$ h, the bent shape is recovered considerably, as can be seen in figure 5(d).

3.2.2 Load–deflection–temperature relationship. The results of the three-point bending test of the SMP sheet for $T_h = T_g$, $t_h = 4$ h and $y_h = 15$ mm are shown in figure 6. The relationship between load and deflection is shown in figure 6(a). As can be seen, load takes a maximum value in the vicinity of a deflection of 10 mm in the pushing process at $T_g + 20$ K (*i*). If the SMP sheet is cooled to room temperature while holding the maximum deflection $y_{max} = 15$ mm, the deformed state is fixed since the SMP is in the glassy region, and load diminishes to zero (*ii*). After cooling to room temperature, the sheet is heated to the holding temperature T_h (*iii*) and is held for the holding time t_h (*iv*). At the terminal point of the lifting process (*v*), residual deflection of 6.5 mm appears.

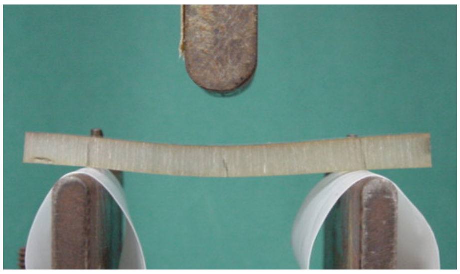
The relationship between deflection and temperature is shown in figure 6(b). While holding the maximum deflection $y_{max} = 15$ mm, which is induced in pushing process (*i*), the sheet is cooled to room temperature (*ii*), heated to the holding temperature T_h (*iii*) and held for the holding time t_h (*iv*). The residual deflection of 6.5 mm appears after the lifting process (*v*). In the heating process with no load (*vi*), deflection decreases and becomes 1.8 mm at the terminal point F at $T_g + 20$ K.

3.2.3 Irrecoverable strain control with a short holding time. In order to evaluate the characteristics of irrecoverable strain control of the SMP sheet subjected to bending, holding strain ε_h and irrecoverable strain ε_p which describe the deformed states, were determined from the bending strains on the surface of the bent sheet. By measuring the radius of curvature r for the neutral surface of the bent sheet at the position of maximum deflection on the photographs shown in figure 5, bending strain ε_h on the surface of the sheet with thickness t was obtained, using $\varepsilon_h = t/2r$, to be 20.8% at $y_h = 15$ mm. The radius of curvature r after heating to $T_g + 20$ K was measured and irrecoverable strain ε_p was obtained in each test. The irrecoverable strain rate S was obtained with equation (1) using holding-bending strain ε_h and irrecoverable strain ε_p. The relationships between S and the holding time t_h obtained

(a) Initial state

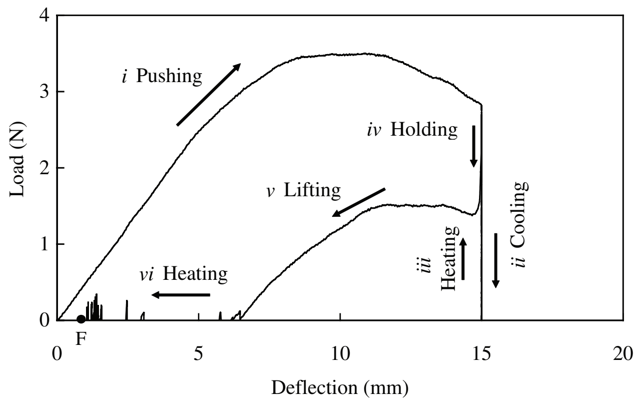
(b) Maximum deflection

(c) Shape-fixed state after cooling

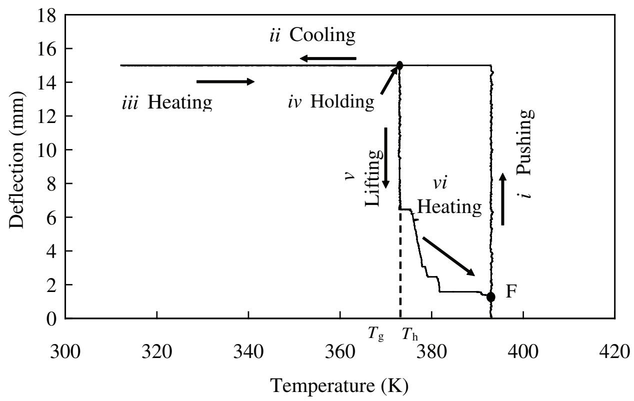


(d) Recovered state after heating

Figure 5. Photographs showing various states of bending for SMP sheet.



(a) Relationship between load and deflection



(b) Relationship between deflection and temperature

Figure 6. Load–deflection–temperature relationship for $T_h = T_g$, $t_h = 4$ h and $y_h = 15$ mm in bending of SMP sheet.

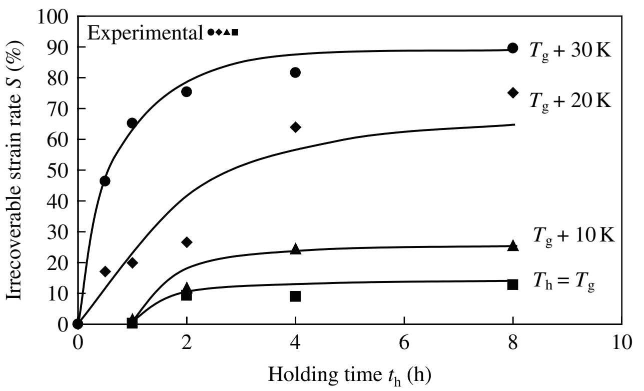


Figure 7. Experimental results of *S* and t_h in bending of SMP sheet.

by the experiment are shown by various symbols in figure 7. In the case of $T_h = T_g$, *S* is 0.3% at $t_h = 1$ h, increases gradually with increasing t_h and becomes 12.8% at $t_h = 8$ h. In the case of $T_h = T_g + 10$ K, *S* is 1.61% at $t_h = 1$ h and 25.6% at $t_h = 8$ h. In the case of $T_h = T_g + 20$ K, *S* is 17.1% at $t_h = 0.5$ h and 75.1% at $t_h = 8$ h. In the case of $T_h = T_g + 30$ K, *S* is 46.4% at $t_h = 0.5$ h and 89.6% at $t_h = 8$ h. It is found from figure 7 that the higher the holding temperature T_h and the longer the holding time t_h, the larger the *S*.

This phenomenon is caused by the thermal motion of the molecular chains (micro-Brownian motion of soft

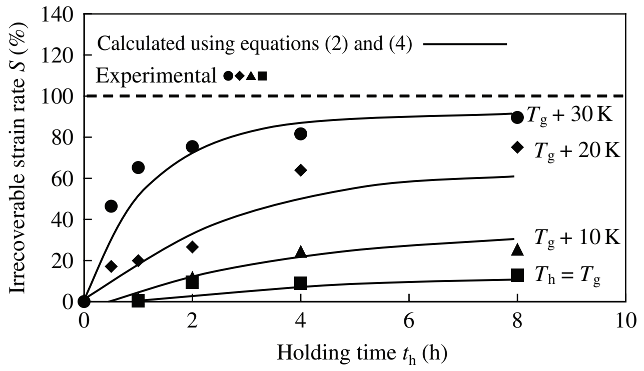


Figure 8. Calculated results of *S* and t_h in bending of SMP sheet.

segments) of the SMP being active at temperatures above T_g, and therefore, reorientation of the molecular chains occurs, resulting in fixing of the bent shape. Nevertheless, *S* does not become 100% until the holding time t_h of 8 h.

Similar to the characteristics of irrecoverable strain control for the film under tension, *S* can be expressed by equation (2). The saturated value S_p, the critical time t_s and the time constant *c* depend on the holding temperature T_h. The characteristic values that approximate the experimental results can be expressed as functions of the holding temperature T_h.

$$\left.\begin{aligned} S_p &= 0.0256(T_h - T_g) + 0.128 \\ c &= -0.175(T_h - T_g) + 6.5 \\ t_s &= -0.065(T_h - T_g) + 1.3 \end{aligned}\right\} . \tag{4}$$

The calculated results using equations (2) and (4) are shown by the solid lines in figure 8. As can be seen, the characteristics of *S* are expressed well by equations (2) and (4). The characteristics of irrecoverable strain control for the sheet subjected to bending show the similar behavior as in the case of the film in tension.

3.2.4 Irrecoverable strain control with a long holding time. The relationship between irrecoverable strain rate *S* and holding time t_h obtained from holding test (ii) for the sheet subjected to bending for a long time is shown in figure 9. As can be seen, when the holding time t_h is long, *S* is 100% at $t_h = 72$ h with $T_h = T_g + 30$ K, at $t_h = 96$ h with $T_h = T_g + 20$ K and at $t_h = 96$ h with $T_h = T_g + 10$ K. In the case of $T_h = T_g$, $S = 95\%$ at $t_h = 96$ h.

Irrecoverable strain rate *S* is shown as a function of holding temperature T_h and holding time t_h obtained from the long-time holding test in figure 10. As can be seen, when T_h is low, t_h needed to reach a certain value of *S* is long, and therefore, the equi-irrecoverable strain rate curve, which connects the same values of *S*, is a right-handed decreasing curve. If the equi-irrecoverable strain rate curve is used, the influence of holding conditions t_h and T_h on *S* can be evaluated at a glance. The equi-irrecoverable strain rate curve can be expressed by the following ellipse:

$$\frac{t_h^2}{t_0^2} + \frac{(T_h - T_g)^2}{T_0^2} = 1, \tag{5}$$

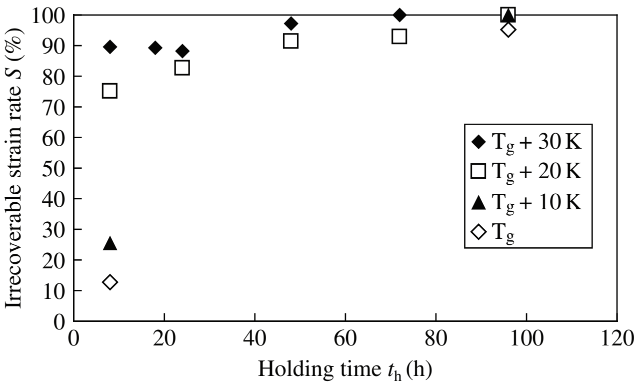


Figure 9. Relationship between S and t_h for SMP sheet in bending by holding for a long time.

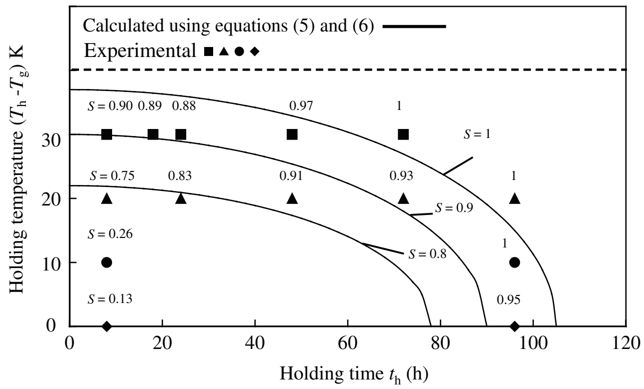


Figure 10. Equi-irrecoverable strain rate curve in bending of SMP sheet.

where t_0 and T_0 denote the major axis and the minor axis of the ellipse, respectively. Thus the equi-irrecoverable strain rate curve for long holding time can be expressed as a function of holding time t_h and holding temperature T_h. The major axis t_0 and minor axis T_0 of the ellipse expressed by equation (5) for the equi-irrecoverable strain rate curve are functions of S as follows:

$$\left.\begin{aligned} t_0 &= 135S - 30 \\ T_0 &= 75S - 38 \end{aligned}\right\}. \qquad (6)$$

The calculated results using equations (5) and (6) are shown by the solid lines in figure 10 for the cases of $S = 80$, 90 and 100%. As can be seen, the characteristics of irrecoverable strain control above S of 0.8 can be approximately expressed by equations (5) and (6). The characteristics of irrecoverable strain control, therefore, can be estimated easily using the equi-irrecoverable strain rate curve.

The influence of holding deflection y_h on the characteristics of irrecoverable strain control is a topic for future studies.

4. Conclusions

Shape recovery and irrecoverable strain control, which present the possibility of obtaining a new shape different from the primary one in polyurethane SMP, were investigated by applying strain at a high temperature, followed by holding under various thermomechanical conditions and heating thereafter. In the experiment, the influence of the strain-holding conditions on the basic properties of shape recovery and irrecoverable strain control was discussed referring to the results of a tension test for the film and a three-point bending test for the sheet. The results are summarized as follows:

1. Irrecoverable strain increases gradually with increasing strain-holding temperature and strain-holding time at holding temperatures above T_g. In order to prevent irrecoverable strain, it is effective to hold the strain at temperatures below $T_g - 10\,K$.
2. The higher the strain-holding temperature and the longer the strain-holding time, the easier the irrecoverable strain appears. In order to use the irrecoverable strain in the fabrication of SMP elements, it is effective to hold the strain at temperatures above $T_g + 20\,K$. The irrecoverable strain rate is described well by an exponential function of the strain-holding time and the strain-holding temperature.
3. In the case of holding the SMP sheet in bending at temperatures above T_g for a long time, the characteristics of irrecoverable strain control above the irrecoverable strain rate of 0.8 can be estimated from the equi-irrecoverable strain rate curve, which is expressed as a function of the holding time and the holding temperature. The equi-irrecoverable strain rate curve is approximately described by an ellipse.

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