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Thermomechanical Properties of Polyurethane-Shape Memory Polymer Foam

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The thermomechanical properties of polyurethane-shape memory polymer foam were investigated experimentally. The results obtained can be summarized as follows. (1) By cooling the foam after deformation at high temperature, stress decreases and the deformed shape is fixed. (2) By heating the shape-fixed foam under no-load, the original shape is recovered. (3) The ratio of shape fixity is 100% and that of shape recovery 98%. (4) Recovery stress increases by heating under constraint of the fixed shape. Recovery stress is about 80% of the applied maximum stress. Relaxed stress at high temperature is not recovered. (5) If the deformed shape is kept at high temperature, the original shape is not recovered. The factors to influence the shape unrecovery are the holding conditions of strain, temperature and time during keeping the deformed shape.

Key words: Shape Memory Polymer, Polyurethane, Shape Fxity, Shape Recovery, Foam

1. INTRODUCTION

Shape memory polymer (SMP) is one of the high-performance materials which have been developed and used in practical applications [1-2]. Since the glass transition temperature T_g of polyurethane-series SMP can be set at around the room temperature and the characteristics of molecular motion differ above and below T_g, the mechanical properties differ markedly above and below T_g [3-4]. The shape fixity and shape recovery exist due to the difference in these properties. The shape fixity and shape recovery properties of SMPs have applications in medical treatment and aerospace engineering fields, etc.

In the present study, as the study of thermomechanical properties of polyurethane-SMP foams, the shape fixity, shape recovery and recovery stress were investigated. In the experiment, by applying the thermomechanical load in combination with loading-unloading and heating-cooling and by investigating the shape fixity and shape recovery, it was found that both properties are very good. The method to obtain the recovery stress effectively in applications to actuators was discussed. The condition to influence the shape recovery was discussed.

2. EXPERIMENTAL METHOD

2.1 Materials and specimens

The material used in the experiment was SMP foam of polyurethane of the polyether polyole series (Diary MF 5520 : produced by Mitsubishi Heavy Industries, Ltd.). The foam was made by chemical foaming. The expansion ratio was about 14 times and the structure was open cell. The foam was produced as slabstock. The specimen was a column with height of 20mm and diameter 20mm. The glass transition temperature T_g was 328K.

2.2 Experimental facility

The shape-memory material testing machine was used for the experiment. The testing machine was composed of the loading system to apply loading-unloading and of the temperature-controlling system to perform heating-cooling. Temperature of the specimen was measured through a thermocouple with diameter of 0.1mm which was in contact with the side of the foam.

2.3 Experimental procedure

In order to investigate the thermomechanical properties, the following four kinds of compression test were carried out. The heating-cooling rate was 5 K/min in each test.

(1) Thermomechanical test

The three-dimensional stress-strain-temperature diagram in the thermomechanical test is shown in Fig.1. At first, ① maximum compressive strain $-\varepsilon_m$ was applied at high temperature $T_h = T_g$+30K. ② Maintaining $-\varepsilon_m$, the specimen was cooled to low temperature $T_l = T_g$-30K. ③ It was held at T_l under no-load condition for 10min. ④ It was heated up to T_h under no-load condition. ⑤ It was held at T_h for 10min. Thermomechanical paths ①～⑤ were repeated 10 times. Strain rate $\dot{\varepsilon}$ was 25%/min.

(2) Recovery-stress test

The three-dimensional stress-strain-temperature diagram in the recovery-stress test is shown in Fig.2. ① At first, maximum compressive stress $-\sigma_m$ was applied at T_h. ② Maintaining the compressive strain $-\varepsilon_m$ at the maximum stress point, the specimen was cooled down to T_l. ③ It was held at T_l under no-load condition for 10min. ④ It was heated to T_h by maintaining the strain $-\varepsilon_m$. ⑤ It was held at T_h for 10min.

(3) New-shape forming test held at high temperature

① At first, maximum compressive strain $-\varepsilon_m$ was applied at T_g+30K. ② The specimen was compressed by using two compression plates in order to keep ε_m constant. ③ The compressed specimen with strain of ε_m was held at a certain constant temperature in a furnace. ④ After the prescribed holding time, the specimen was taken out from the furnace and the holding attachment was removed. ⑤ The shape of the specimen was recovered by heating at T_g+30K and height of the

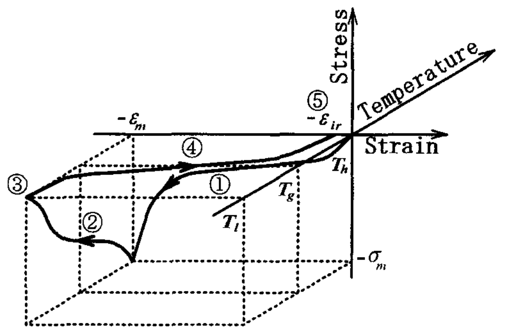

Fig.1 Three-dimensional stress-strain-temperature diagram showing the loading path in the thermomechanical compression test

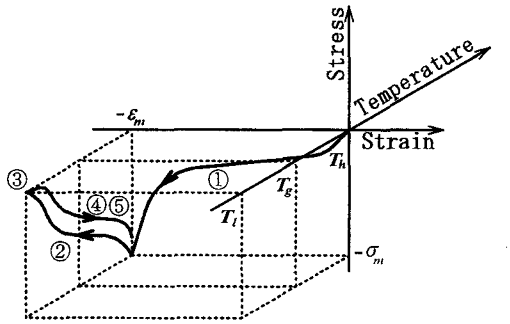

Fig.2 Three-dimensional stress-strain-temperature diagram showing the loading path in the recovery stress test

specimen was measured. By this procedure, unrecoverable strain ε_p was obtained.

3. RESULTS AND DISCUSSION

3.1 Shape fixity and shape recovery

Rate of shape fixity R_f and rate of shape recovery R_r were defined by the following equations

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100 \qquad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_{ir}}{\varepsilon_m} \times 100 \qquad (2)$$

where ε_u and ε_{ir} represent the strain obtained after holding no-load condition below T_g and the strain obtained after holding no-load condition above T_g, that is, unrecoverable strain, respectively.

(1) Stress-strain relationship

The compressive stress-strain curves obtained by the thermomechanical test for ε_m= 78% are shown in Fig.3. In Fig.3, N denotes the number of cycles. As can be seen, stress increases in proportion to strain till a strain of 10%, yielding appears in the vicinity of a strain of 10%, stress increases gradually thereafter till a strain of 60% and the slop of the curve becomes steep above a strain of 60%. In the region of the stress plateau for strain from 10% to 60%, buckling of cells propagates in the axial direction of compression. In the upswing region above a strain of 60%, the material is compressed uniformly and deformation resistance increases. With respect to the stress-strain curves in the loading process ①, stress decreases a little from N =1 to N =2 and decreases slightly thereafter. In the cooling process ②, stress disappears perfectly at temperature T_l. Therefore ε_m is maintained and $\varepsilon_u = \varepsilon_m$, resulting in a rate of shape fixity R_f of 100%. In these processes, the influence of friction at both end surfaces of the specimen on the deformation was not observed.

(2) Stress-temperature relationship

The stress-temperature curves obtained by the thermomechanical test are shown in Fig.4. As can be seen , stress decreases in the cooling process ②. Just after the start of cooling, stress decreases due to stress relaxation at high temperature. In the middle stage of the process ②, stress decreases due to thermal contraction based on decrease in temperature. Since a crosshead is held constant during the process ② and the compressed SMP foam contracts thermally, stress decreases. In the latter stage of the process ②, the amount of decrease in stress is large. This occurs due to the following cause. Since the modulus of elasticity of SMP is quite large at temperatures below T_g [3-4], the rate of variation in thermal stress increases due to thermal contraction based on decrease in temperature. As a result, the slope of the curve becomes steep at low temperature. The stress-temperature curves do not change under repetition.

(3) Strain-temperature relationship

The strain-temperature curves obtained by the thermomechanical test are shown in Fig.5. As can be seen, in the heating process ④ , strain is recovered significantly in the vicinity of T_g. Since the micro-Brownian motion of soft segments of SMP is frozen in the glassy region at temperatures below T_g, strain maintains ε_m. Since the micro-Brownian motion becomes active when the material is heated up to temperatures in the vicinity of T_g, strain is recovered.

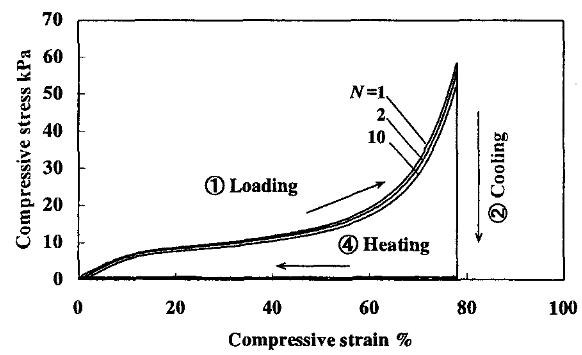

Fig.3 Stress-strain curves in the thermomechanical test

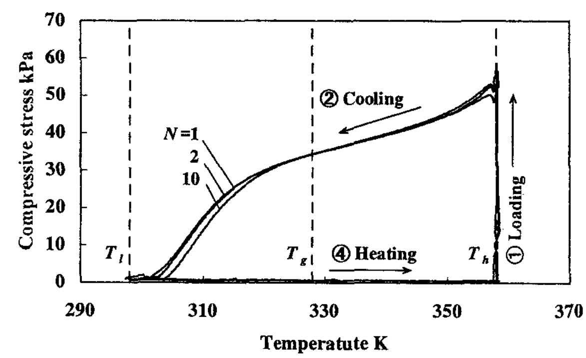

Fig.4 Stress-temperature curves in the thermomechanical test

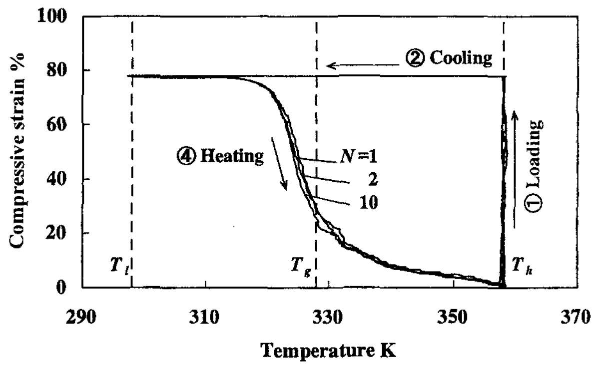

Fig.5 Strain-temperature curves in the thermomechanical test

The strain-temperature curves do not change under repetition.Unrecoverable strain remaining after heating is small without depending on the number of cycles, and rate of shape recovery R_r is 99%.

3.2 Recovery stress

(1) Dependence on strain rate

The recovery stress test for various strain rates $\dot{\varepsilon}$ under a constant maximum compressive stress σ_m =100kPa was carried out. The stress-strain curves and stress-temperature curves obtained by the test are shown in Fig.6 and Fig.7, respectively. As can be seen in Fig.6, the smaller the $\dot{\varepsilon}$ in the loading process ①, the smaller the deformation resistance and the larger the strain at the point of maximum stress. As can be seen in Fig.7, the smaller the $\dot{\varepsilon}$, the larger the recovery stress obtained in the heating process ④. This occurs due to the fact that the influence of stress relaxation just after the start of cooling is small if $\dot{\varepsilon}$ is small. If $\dot{\varepsilon}$ is small, the SMP foam is compressed slowly for a long time in the loading process ①, it becomes dense and large compressive strain appears. As a result, stress relaxation is small. The temperature at which stress increases markedly in the heating process ④ is higher than that at which stress decreases markedly in the cooling process ② and is closer to T_g by about 10K. This behavior occurs due to the fact that, though the micro-Brownian motion of soft segments of SMP is frozen at low temperature and molecular chain can not move, the micro-Brownian motion becomes active by heating up to the vicinity of T_g and recovery stress appears gradually with an increase in temperature.

(2) Dependence on maximum stress

The recovery stress test at $\dot{\varepsilon}$ =2.5%/min in the loading process ① for various maximum compressive stresses σ_m was performed. Considering to use large recovery force and driving force in applications of SMP foam elements, the values of 100kPa, 1MPa and 10MPa were selected for σ_m. The relationship between the obtained recovery stress and the applied maximum stress is shown in Fig.8. As can be seen, recovery stress is proportional to applied maximum stress. Recovery stress is about 80% of the applied stress. In the case of recovery stress for SMP sheet and film under tension obtained by heating under constant strain, recovery stress is about 50% of the applied stress. Therefore, it must be a very effective method to obtain recovery stress by compressing SMP foam. Since large change in volume can be obtained for SMP foam elements, they can be applied to the easily portable energy sources to use recovery stress.

3.3 Unrecovery by holding at high temperature

In the process of the present study, it was found that, if SMP foam was deformed and the deformed shape was held for a long time above T_g, unrecoverable deformation appeared. That is, it was found that the deformed shape was fixed. This phenomenon is called secondary-shape forming. In order to investigate the phenomenon, the secondary-shape forming test by keeping the deformed shape above T_g for a certain time was carried out. The relationship between a ratio of unrecoverable strain ε_p to applied maximum strain ε_m ($\varepsilon_p/\varepsilon_m$) and the holding time obtained by the test is shown in Fig.9. If the ratio is zero, secondary-shape forming does not appear. If the ratio is one, ε_m remains as ε_p. Therefore, $\varepsilon_p/\varepsilon_m$ expresses a rate of secondary-shape forming or a rate of unrecovery.

As can be seen in Fig.9, ε_p appears slightly at holding temperature T_g. This ε_p may appear due to the fact that weak cell in SMP foam collapses and the initial shape is not recovered. On the other hand, ε_m remains almost as ε_p at holding temperature T_g+60K. The reason why this ε_p appears is not due to collapse of cell but due to secondary-shape forming. Therefore, if strain is kept above T_g, secondary-shape forming may appear easily. In the case of holding temperature of T_g+30K, ε_p increases in proportion to the holding time. Therefore, secondary-shape forming appears when the material is held above T_g for a long time. In the case of both T_g+30K and T_g+60K, ε_p is large as ε_m is large. From these results, it is ascertained that the factors to affect secondary-shape forming are the holding strain, temperature and time. The

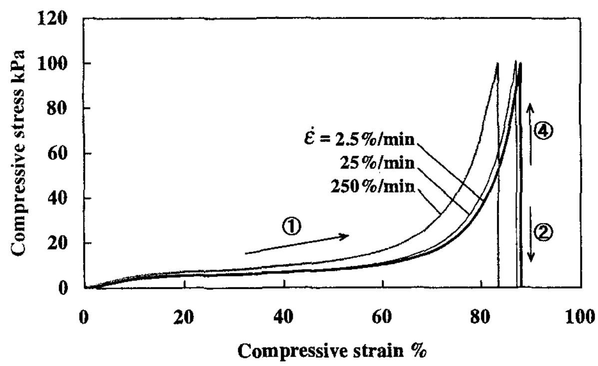

Fig.6 Stress-strain curves in the recovery-stress test

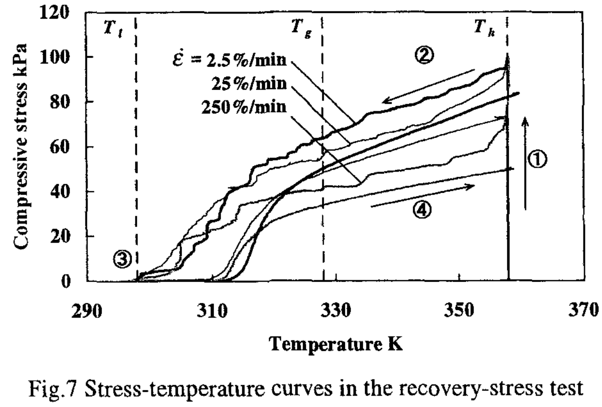

Fig.7 Stress-temperature curves in the recovery-stress test

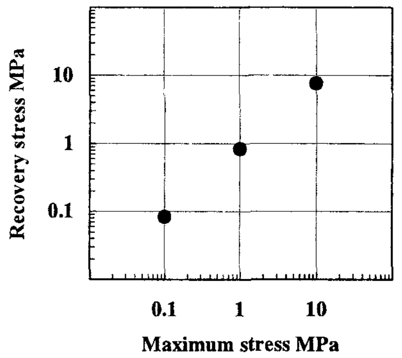

Fig.8 Relationship between recovery stress and maximum stress

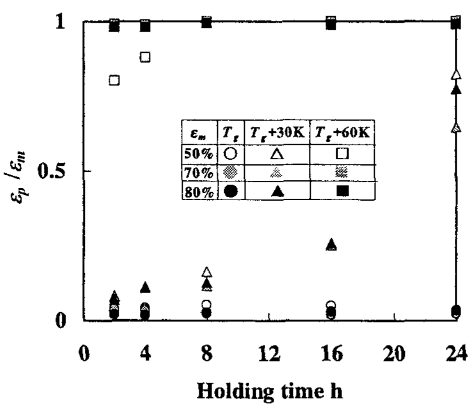

Fig.9 Relationship between unrecovery ratio $\varepsilon_p/\varepsilon_m$ and holding time at various holding temperatures and maximum stress

cause of secondary-shape forming can be considered as follows. In the region of temperature above T_g, thermal motion of molecular chain (micro-Brownian motion) is active and therefore reorientation of molecular chain progresses by holding large strain for a long time. In order to avoid secondary-shape forming for the deformed SMP foam, it is important to keep the foam under the appropriate condition by considering these conditions. One of the methods to prevent secondary-shape forming is to keep the foam in the region of temperature below T_g. In the region of temperature below T_g, secondary-shape forming does not appear and both the rate of shape fixity and that of shape recovery are high. Therefore, holding at low temperature must be effective in applications of SMP foam elements.

4. Conclusions

Applying various thermomechanical loadings to polyurethane-SMP foams, the thermomechanical properties of the material were investigated. The results obtained can be summarized as follows.

(1) If the SMP foam deformed above T_g is cooled down to below T_g, stress diminishes and the deformed shape is fixed. In the cooling process, stress decreases markedly in the region of temperature below T_g.
(2) If the SMP foam fixed at the deformed shape is heated under no load, shape is recovered. In the heating process, strain is recovered markedly at temperatures in the vicinity of T_g.
(3) The rate of shape fixity and that of shape recovery are 100% and 99%, respectively. Both rates do not depend on the number of cycles.
(4) If the SMP foam deformed above T_g is cooled down below T_g followed by heating under holding the deformed shape, recovery stress appears. Recovery stress is about 80% of the applied compressive stress. If stress relaxation appears, the relaxed stress is unable to be used as recovery stress.
(5) If the deformed SMP foam is held above T_g, secondary-shape forming appears. The factors to affect secondary-shape forming are holding strain, temperature and time.

REFERENCES
[1] S. HAYASHI, *Int. Progr. Urethanes,* **6**, 90-115 (1993).
[2] M. Irie, Shape memory polymers, In : Otsuka, K. and Wayman, C. M. eds., *Shape Memory Materials,* 203-19 (1998), (Cambridge University Press, Cambridge).
[3] T. Takahashi, N. Hayashi and S. Hayashi, *J. Appl. Polym. Sci.*, **60**, 1061-69 (1996).
[4] H. Tobushi, T. Hayashi, N. Ito, S. Hayshi and E. Yamada, *J. of Intell. Mater. Syst.& Struct.*, **9**, 127-36 (1998).

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