Constitutive Modeling of Shape Memory Fibers and Its Application

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Abstract

Some segmented polyurethane polymers are known to have shape memory function, i.e., when a certain temperature is given to them, they deforms into a memorized shape from any temporary ones. In this study, polyurethane polymers with such shape memory function were spun into fibers using the conventional extrusion process to investigate the feasibility of making smart fibers and textiles with shape memory function. The performance of the spun fibers was evaluated focusing on the shape memory function using the thermo-mechanical testing. Finally an attempt was made to formulate a constitutive equation for shape memory fibers using visco-elasticity, aiming to provide an effective tool of designing smart textiles using the shape memory fibers.

Keywords: shape memory polymer; polyurethane; smart fiber; visco-elastic theory

1. Introduction

There have been various attempts made to develop smart materials which are responsible to certain stimuli such as temperature, electric current, acidity, etc. Temperature sensitive materials are materials that can change their physical shape, e.g., from strained shapes to an unstrained shape, as the temperature in them reaches at specific one. This unusual deformation behavior was observed in shape memory polymers (SMPs) and metal alloys. Many researches [1-4] have been dedicated to develop SMPs due to their good processibility, light weight, low cost, and high recovery strain, which can be more than 100%, whereas shape memory metal alloys have the same function within the small deformation, e.g., several percentages at most.

A typical behavior of SMP is illustrated in Fig. 1. Thermoplastic SMPs can be processed to have permanent shapes using thermo-processes. At higher temperature than a specific one (this temperature is referred to as the transition temperature, T_{tr}), SMP is mechanically deformed into a temporary shape (stage 1 in Fig. 1). The temporary shape is now fixed by lowering the temperature (stage 2 in Fig. 1) and releasing the stress (stage 3 in Fig. 1). At this moment, the polymer molecules in SMP also tend to return to the permanent shape without deformation; however since the rigidity in the molecules was increased by lowering the temperature, they can not take up all the deformation, thereby leaving the temporary shape fixed. Here the fixity can be defined as the difference in shapes after stage 1 and 3. The fixity can be a criterion to assess the shape memory performance because large fixity implies better micro-phase separation in SMP. Upon heating the rigidity of polymer chains in the soft-segment decreases, thereby the frozen stress becomes activated such that SMP recovers all the deformation and returns to the permanent shape (stage 4 in Fig. 1). Here the recovery strain can be another criterion to assess the shape memory performance.

For the thermo-mechanical characterization of SMP, tensile testing instruments with a specific control program has been used [2,5]. Frequently the fixity and recovery strain only have been measured because the general tensile testers can not trace the cyclic deformation in Fig. 1, making it difficult to characterize the transition behavior of SMPs [6-7]. In the current study DMTA was utilized to characterize the transition behavior of SMPs, which has not been reported so far to authors' knowledge.

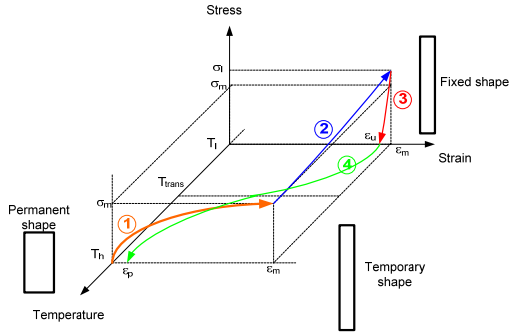


Fig. 1. A typical thermo-mechanical behavior of SMP.

Concerning constitutive modelling of SMPs, a few reports have been published [8-10]. Linear and nonlinear viscoelastic theories were applied to describe their thermo-mechanical behavior [8-9]. Four-elements mechanical unit (spring, dashpot, frictional device) was used to derive a differential constitutive equation. In determining the material properties for the constitutive equation, it was assumed that modulus, viscosity, and other parameters are decayed exponentially according to temperature. Liu et al [10] attempted to develop a constitutive equation based on the thermodynamic concepts of entropy and internal energy. Adopting the concept of 'frozen' strain, they demonstrated the utility of their model by simulating the strain and stress recovery under various flexible constraint levels.

The present study adopted the rheological approach using the linear visco-elastic theory as the first trial; however we did not

rely on the differential equation as in [8-9]. Instead, the relaxation modulus was measured in the various temperatures and used to build the master curve. The details for this will be provided after discussing experiments for the characterization and melt-spinning of SMP.

2. Experimental

There are many SMPs which are responsible to temperature. In this research, a sample material, which was synthesized by one step process with 4,4'-diphenylmethane diisocyanate, poly(alkylene adipate)-based polyol and 1,4-butanediol (by Hosung Chemex Co. in Korea), was chosen to investigate the thermo-mechanical behavior of both SMP and its spun fibers.

2.1 Thermal analysis

For SMP with the soft segment that can crystallize to an extent, its transition temperature is determined by the melting temperature (Tm) of the soft segment, while the glass transition temperature (Tg) plays the same role for SMP with the soft segment that can not form crystallite. In the current study, Tm was determined as the transition temperature because the soft segment can crystallize to an extent as demonstrated in Fig. 2. Note that Tm of the soft segment was determined to be 33.5 ^{o}C.

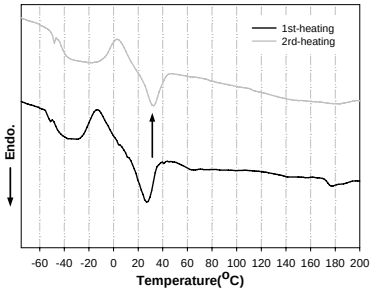


Fig. 2. DSC thermodiagram of samples

2.2 Spinning of the SMPs

The sample SMP was spun into fibers using the conventional melt extrusion process. Considering the rheological properties including the melt index, the extrusion conditions were set up in Table 1.

Table 1 Spinning conditions for SMPS.

Feeding zone℃	Zone 2	Zone 3	Die	Winding Speed (RPM)	Screw Speed (RPM)
175℃	180℃	185℃	190℃	350	14

2.3. Thermo-mechanical characterization

As shown in Fig. 1, the thermo-mechanical test of SMPs consists of four steps; 1) deforming at the higher temperature than the transition one, 2) cooling down to the lower temperature maintaining the strain constant, 3) releasing the stress, and 4) heating up to the high temperature keeping the stress zero. In this research, DMTA was utilized to impose those four steps of thermo-mechanical deformation. In the third step, the load should be released continuously, however since the current setup of DMTA does not allow such linear drop, stepwise drops were programmed to simulate the linear drop. Two deformation modes, i.e. bending and tensile modes, were adopted for the thermo-mechanical characterization. The bending mode was applied to film specimens for small deformation case; whereas the melt spun fibers were tested in the tensile mode.

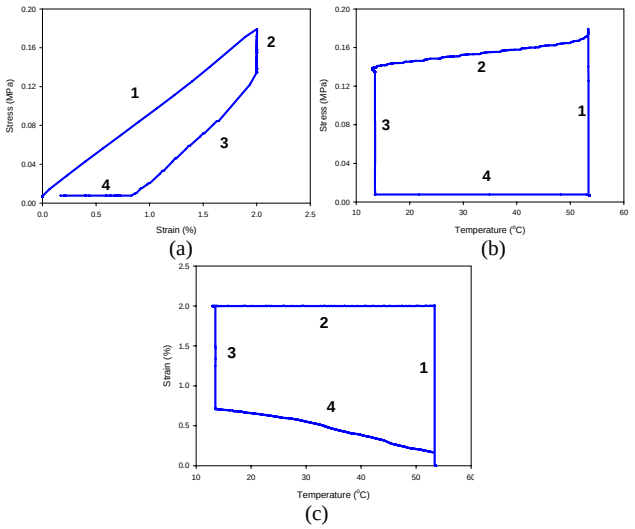
3. Results and discussion

3.1 Characterization results of the SMPs

The thermo-mechanical characterization of the sample SMP was performed using the rectangular specimens in the bending mode and illustrated in Fig. 3. Note that the numbers inside the plot windows indicate the testing steps in Fig. 1. For this small strain case, the linear relationship was observed between stress and strain at the first step of the thermo-mechanical test. In the second step, the effect of the thermal shrinkage was not clearly observed. Were it involved, the constant strain condition in this step might increase the stress due to the restricted thermal contraction. For the moment, it is not clear why the thermal contraction was not manifested. The fixity in this sample was not good since about 50% strain was recovered after the cooling process. This may indicate that in the sample SMP the hard and soft segments were not separated well. This fact is also confirmed from temperature and strain plot in Fig. 3. Strain recovery rate is almost constant and very similar to the modulus at high temperature, indicating that the phase separation is not complete. Note that once the heated sample was deformed, the stiffness in the cooled sample was deteriorated (see parallel slope in 1 and 3 in Fig. 3. (a)). As the maximum strain imposed increases, this tendency remains as shown in Fig. 4. The shape memory performance of the sample SMP is summarized in Table 3.

Table 2. Thermo-mechanical test condition of SMPs.

	Input	Constraint	Output
1st step	strain	strain rate: 5%/min, temp: T_{tr} + 20^{o}C	stress
2nd step	cooling	strain fixed: temp rate: of 4^{o}C/min	stress
3rd step	unloading	temp: Ttr – 20^{o}C	strain
4th step	heating	zero load temp rate: 4^{o}C/min	strain



(a) (b)

(c)

Fig. 3. Thermo-mechanical test result of sample SMP. (a) stress-strain curve, (b) stress-temperature, (c) strain-temperature curve.

The thermo-mechanical behavior of the fibers spun from the SMP was investigated using DMTA in tensile mode. The maximum strain was increased to 25%, 50% and 80%. As shown in Fig. 5, the hysterisis becomes more pronounced as the maximum strain increases. The nonlinear behavior was also

observed for this large deformation case. Note that the shape memory performance such as the fixity and the recovery are very similar to the small deformation case, implying that strain hardening/softening mechanism was not involved in the current SMP.

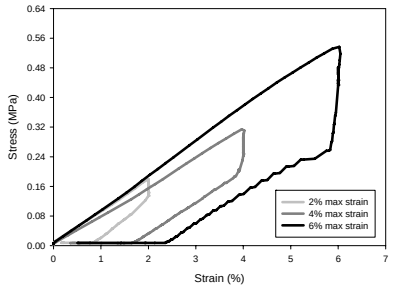


Fig. 4. Themo-mechanical deformation behavior of sample SMP.

Table 3. Shape memory performance of two SMPs.

ε_m(%)	ε_u(%)	ε_p(%)	R_r (%)	R_f (%)
2	0.7114	0.1667	91.665	35.57
4	1.434	0.3603	90.9925	35.85
6	2.0739	0.51	91.5	34.565

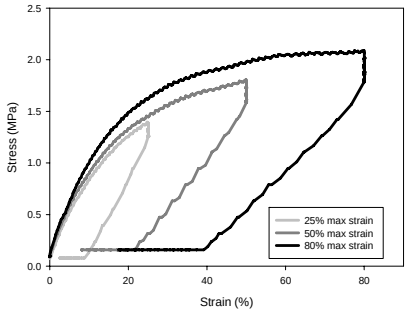


Fig. 5. Thermo-mechanical behavior of SMP spun fibers.

3.2. Constitutive modelling of SMP

The linear viscoelastic theory was applied as the first trial. Since the 'linear' theory implies its limitation to the small deformation, we focus on the description of thermo-mechanical behavior of SMPs within the small deformation range. For the large deformation case (see the experiments for the shape memory fibers), a nonlinear viscoelastic model will be adopted and presented in a future.

The linear visco-elastic theory can be described by the hereditary integral derived by Boltzmann superposition principle as follows.

$$\sigma(t) = \int_{-\infty}^{t} E\left(\xi - \xi'\right)\frac{d\varepsilon}{ds}ds \qquad (1)$$

where σ , ε , and E are stress, strain, and the relaxation modulus, respectively. Note that ξ and ξ' are the reduced or intrinsic time, which was introduced to describe temperature varying deformation behavior, as follows.

$$\xi = \int_{-\infty}^{t} \frac{d\tau}{a_T(\tau)}, \quad \xi' = \int_{-\infty}^{s} \frac{d\tau}{a_T(\tau)} \qquad (2)$$

Here, a_T is the shift factor which can be determined by shifting the relaxation curve at several temperatures to the reference temperature.

For the thermo-mechanical description of SMP, the relaxation modulus was measured by varying the temperature from 13.5 to 53.5 ^{o}C as shown in Fig. 6. It is observed that the relaxation time becomes shorten as the temperature increases. The master curve of the relaxation modulus was obtained at a reference temperature (here, T_{tr}=33.5 ^{o}C) by calculating the shift factor, which was determined using the conventional method by plotting the relaxation curve in log time and log modulus chart as shown in Fig. 7. Then, the shift factor was used for the calculation of the reduced time under the varying temperature condition. Finally the relaxation curve at the reference temperature was fully determined using the shift factors. The relaxation curves in Fig.6 were re-calculated using the master curve, the shift factor, and Eqn (1), demonstrating that the 'thermo-rheologically simple material' assumption for SMP in this study is acceptable as shown in Fig. 8.

3.3. Simulation results

Temperature varying properties can be simulated using the master curve and shift factor with Eqn (1). In this simulation, the stress in Eqn (1) was assumed to be generated by the mechanical strain only, which can be obtained by subtracting the thermal strain from the total strain. For the thermal strain calculation, the thermal expansion/contraction coefficient (11.6E-5 (/K)) was adopted from the literature [8].

Fig. 9 shows the simulation result of thermo-mechanical behaviour of SMP. The second step in this simulation does not show the increase of the stress, due to the small thermal strain involved. In the experiment the stress were not relaxed quickly than in the simulation, deducing that the master curve for the relaxation modulus at the reference temperature may not be accurate enough to describe the temperature varying relaxation modulus. As the temperature increases after the second and third steps (the fixation step of the strain), the strain recovery process expedites. Note that the strain recovery is not linear with the increased temperature, instead it increases significantly at the high temperature beyond the transition one. This result is consistent with the relaxation curve in Fig. 6, i.e., the relaxation modulus drops significantly in the high temperature beyond the transition temperature. In conclusion, the linear viscoelastic model seems to describe the thermo-mechanical behavior of SMP such as the fixity and recovery of the strain; however, in the third step the simulation result is not comparable with experiment (see the third step in Fig. 3 and Fig. 9), the reason of which should be explored as follows.

The relaxation modulus in Fig. 6 shows about three order difference in modulus between T_l (=13.5^{o}C) and T_h (=53.5^{o}C). Such difference brings out different paths in the stress and strain relationship according to the temperature, i.e., the slope of stress and strain at T_h is smaller than one at T_l, imparting the fixity and recovery properties to SMP. This consideration can be also confirmed by the simulation result in Fig. 9. In contrast, the thermo-mechanical test in Fig. 4 does not reflect this difference in modulus at T_l and T_h, concluding that other softening mechanism may happen to SMP during its thermal treatment. In the mechanical modelling using the linear visco-elastic theory, this reduced rigidity during the thermal treatment was not considered

so that the discrepancy between experiment and theory was not avoidable.

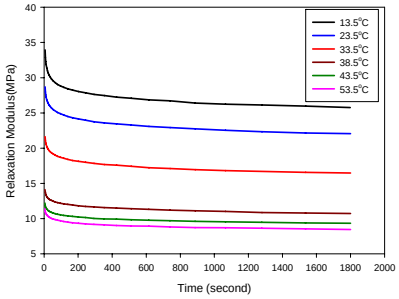


Fig. 6. Relaxation curve of shape memory polymer according to temperature.

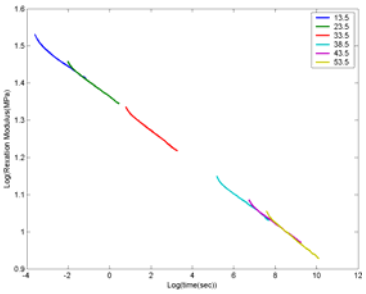


Fig. 7. The shifted curve of stress relaxation curve to build the master curve at a reference temperature.

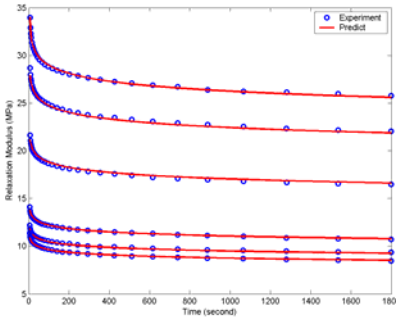


Fig. 8. Validation of 'thermorheologically simple material assumption' for a shape memory polymer.

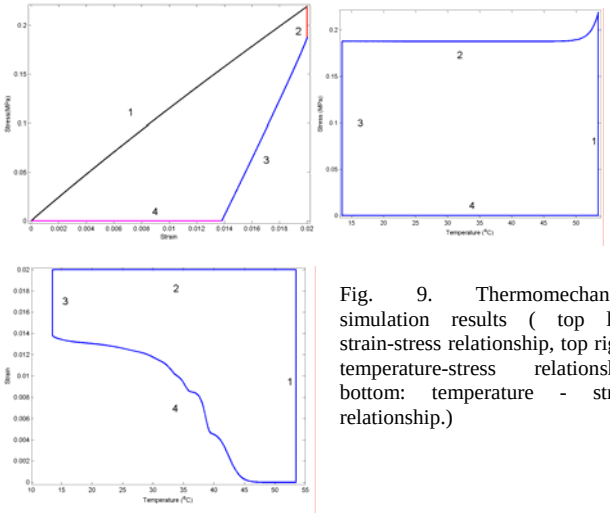


Fig. 9. Thermomechanical simulation results (top left: strain-stress relationship, top right: temperature-stress relationship, bottom: temperature - strain relationship.)

4. Conclusions

The thermo-mechanical behavior of the SMPs and their fibers were characterized using DMTA. It was observed that the fibers spun from the SMPs behaved in the same way as their bulk form did, thereby concluding that the smart fibers with the smart functions such as shape fixity and recovery according to temperature can be manufactured from SMP. To model the thermo-mechanical behavior of SMP, the linear visco-elastic theory was applied using the time-temperature supposition and the reduced or intrinsic time concept. It was found that in general the linear visco-elastic model can predict the characteristics of SMPs, in particular the fixity and recovery in the small deformation regime, however the discrepancy between experiment and calculation was observed, main source of which needs to be explored.

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References

[1] A. Lendlein, S. Kelch, Shape-Memory Polymers, Angew Chem Int Edit, 41(12), 2034(2002).

[2] H.Tobushi, H. Hashimoto, N. Ito, Shape Fixity and Shape Recovery in a Film of Shape Memory Polymer of Polyurethane Series, J Intel Mat Syst Str, 9(2), 127(1998).

[3] X.L. Meng, Y.F. Zheng, Z. Wang, L.C. Zhao, Shape memory properties of the $Ti_{36}Ni_{49}Hf_{15}$ high temperature shape memory alloy, Mater Lett, 45(2), 128(2000).

[4] A. Lendleing, R. Langer, Biodegradable, Elastic Shape-Memory Polymers for Potential Biomedical Applications, Science, 296(5573), 1673(2002).

[5] H. Tobushi, H. Hara, E. Yamada, S. Hayashi, Thermomechanical properties in a thin film of shape memory polymer of polyurethane series, Smart mater struct, 5(4), 483(1996).

[6] J. W. Cho, Y. C. Jung, Y.-C. Chung, B. C. Chun, Improved mechanical properties of shape-memory polyurethane block copolymers through the control of the soft-segment arrangement, J Appl Polym Sci, 93(5), 2410(2004).

[7] B. K. Kim, S. Y. Lee, J. S. Lee, S. H. Baek, Y. J. Choik, J. O. Lee, M. Xu, Shape-memory behavior of segmented polyurethanes with an amorphous reversible phase: The effect of block length and content, Polymer , 39(13), 2803(1998).

[8] H. Tobushi, T.Hashimoto, S.Hayashi, E.Yamada, Thermomechanical constitutive modeling in shape memory polymer of polyurethane series, J Intel Mat Syst Str, 8, 711(1997).

[9] H. Tobushi, K. Okumura, S.Hayashi,N.Ito, Thermomechanical constitutive model of shape memory polymer, Mech Mater, 33, 545(2001).

[10] Y. Liu, K.Gall, M.L.Dunn, A.R.Greenberg, J.D.Diani, Thermomechanics of shape memory polymers: uniaxial experiments and constitutive modeling, Int J Plasticity, 22, 279(2006).