International Journal of Modern Physics B
Vol. 23, Nos. 6 & 7 (2009) 1248–1253

A GLASS TRANSITION MODEL FOR SHAPE MEMORY POLYMER AND ITS COMPOSITE

BO ZHOU[1,2,*] and YAN-JU LIU[2,†]

[1]*College of Aerospace and Civil Engineering, Harbin Engineering University, 145 Nantong Street, Harbin, Heilongjiang Province 150001, People's Republic of China*
[2]*Department of Aerospace Science and Mechanics, Harbin Institute of Technology, 92 Xidazhi Street, Harbin, Heilongjiang Province 150001, People's Republic of China*
[*]*zhoubo@hrbeu.edu.cn*, [†]*yj_liu@hit.edu.cn*

XIN LAN[3], JIN-SONG LENG[3,‡] and SUNG-HO YOON[4,§]

[3]*Center for Composite Materials and Structures, Harbin Institute of Technology, 2 Yikuang Street, Harbin, Heilongjiang Province 150080, People's Republic of China*
[4]*School of Mechanical Engineering, Kumoh National Institute of Technology, 2 Yangho-Dong, Gumi, Gyeongbuk 730-701, Korea*
[‡]*lengjs@hit.edu.cn*, [§]*shyoon@kumoh.ac.kr*

Received 28 November 2008

As novel smart materials, shape memory polymer (SMP) and its composite (SMPC) have the ability to regain its original shape after undergoing significant deformation upon heating or other external stimuli such as light, chemic condition and so on. Their special behaviors much depends on the glass transitions due to the increasing of material temperature. Dynamic Mechanical Analysis (DMA) tests are performed on the styrene-based SMP and its carbon fiber fabric reinforced SMPC to investigate their glass transition behaviors. Three glass transition critical temperatures of SMP or SMPC are defined and a method to determine their values from DMA tests is supposed. A glass transition model is developed to describe the glass transition behaviors of SMP or SMPC based on the results of DMA tests. Numerical calculations illustrate the method determining the glass transition critical temperature is reasonable and the model can well predict the glass transition behaviors of SMP or SMPC.

Keywords: Shape memory polymer; shape memory polymer composite; glass transition model.

1. Introduction

Shape memory polymer (SMP) is one of the promising smart materials, which is intensively investigated by the researchers from various countries or regions due to its excellent shape memory effect[1,2]. The unconstraint recovery strain of SMP is as high as or even more than the order of 100%, while that of shape memory alloy is less than the order of 10%. SMP is with not only superexcellent shape memory effect but also low density, easy shaping procedure, easy controlling the recovery temperature, low cost and so on. Various SMP resins have been reported in the recent literatures. The thermoplastic polyurethane-based SMP is the normal kind of SMP resin in practical applications for its glass transition temperature can be easily tailored from -30°C to 70°C by the control of chemistry and structure[3]. The thermoset epoxy-based SMP resin has also been researched due to its high glass transition temperature of approximate 80-110°C. The styrene-based SMP is another kind of thermoset SMP resin with the glass transition temperature of 80°C [4-5]. The thermoset cyanate-based ester SMP resin has the extremely high glass transition temperature from 135°C to 238°C, which can meet some special practical requirements[6]. Shape memory polymer composite (SMPC) was also fabricated and investigated in order to improve the performances of SMP such as strength, stiffness, conductivity and so on. Three kinds of SMPC have been being researched, which are powder filled SMPC[7-8], short-cut fiber reinforced SMPC[9,10] and fiber reinforced SMPC[11].

Both shape memory effects in SMP and SMPC are the results of the glass transition in the materials due to the change of material temperature. SMPC will play an important role in deployable structures, such as deployable space antenna, truss and solar arrays in space industry, due to its superexcellent shape memory effect. It is very necessary to experimentally investigate and theoretically model the glass transition behaviors of SMP and SMPC.

In this study, the DMA tests are operated on the styrene-based SMP and its carbon fiber fabric reinforced SMPC to investigate the influence of the reinforcement of SMPC on the material properties. Three glass transition critical temperatures of SMP or SMPC are defined and a new method to determine the glass transition critical temperatures of SMP or SMPC is proposed based on the DMA test. A new glass transition model is developed to predict the glass transition behaviors of SMP or SMPC based on the DMA test. Numerical calculations are carried out to illustrate that the method is reasonable and the model is effective.

2. Experiment Procedures

The matrix and reinforcement of SMPC are the thermoset styrene-based SMP and plain-weave carbon fiber fabric. The SMPC is fabricated through standard fiber reinforced composite materials fabrication techniques, curing of a preimpregnated fabric. The SMPC with the reinforcement of three-plies plain weave is used for all the tests in this study. In order to investigate the influences of the reinforcement on the characteristics of SMPC, the pure styrene-based SMP specimen is also cured with the same temperature and time as SMPC specimen.

In order to investigate the glass transition behaviors of SMP and SMPC, DMA tests are respectively operated on them under the same testing conditions. The experimental equipment is Dynamic Mechanical Analyzer (NETZSCH, DMA242C) and the test-model is three-point bending model with the span of 40mm. The length, width and thickness of the rectangular-section specimen are 50mm, 9mm and 3mm respectively. The initial static load is 2N and the frequencies include 0.2Hz, 1.0Hz and 5Hz. The scanning range of temperature is 0-120°C and the heating rate is 2°C/min.

3. Experimental Results

The experimental results at the frequencies of 0.2Hz, 1.0Hz and 5.0Hz have the similar reasonable errors, so only the results at the frequency of 1.0Hz are given out for discussion in this paper. The DMA test results of SMP and SMPC are shown in Fig. 1, where the curves of elastic modulus versus temperature and tangent delta versus temperature of SMPC and SMP are plotted.

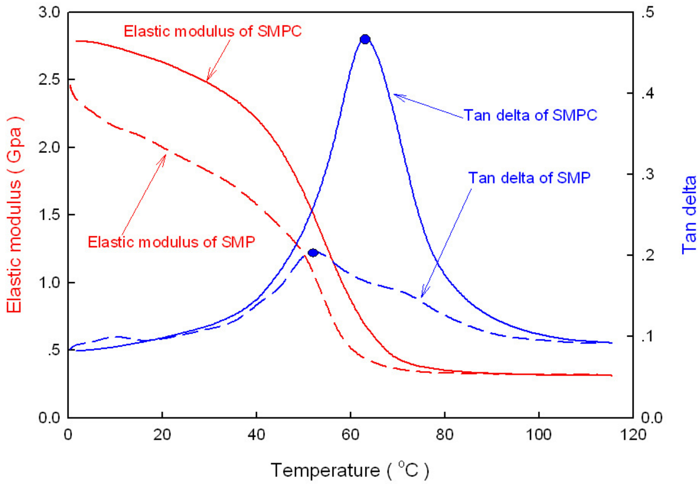

Fig. 1. Experimental curves from DMA tests.

The curves in Fig. 1 show that the elastic modulus of SMPC is higher than that of SMP in the low-temperature region, which explains the reinforcement in SMPC improve the material stiffness. While the elastic modulus of SMP and SMPC are almost same in the high-temperature region. This may be because the matrix material, SMP, becomes soft and separates from the reinforcement at the high temperature, which makes the reinforcement can not improve the material stiffness.

4. Definition of Glass Transition Critical Temperature

It is very important to correctly define and determine glass transition critical temperatures of SMP and SMPC for their practical applications. Ordinarily, one glass transition critical temperature, glass transition temperature, T_g, is defined. It is often determined by the peak point of the curve of the tangent delta versus temperature from DMA test, shown in Fig. 1.

During the process of the glass transition of SMP or SMPC, the material properties rapidly change with the increasing of temperature. So it is more reasonable to define the glass transition critical temperatures according to the relationship of the temperature derivative of elastic modulus and temperature. The curve of temperature derivative of elastic modulus versus temperature can be obtained through numerical differential calculations from the curve of elastic modulus versus temperature from DMA test. Figure 2 shows the curves of temperature derivative of elastic modulus versus temperature of SMPC, which is obtained from the curves of elastic modulus versus temperature of SMPC in Fig. 1.

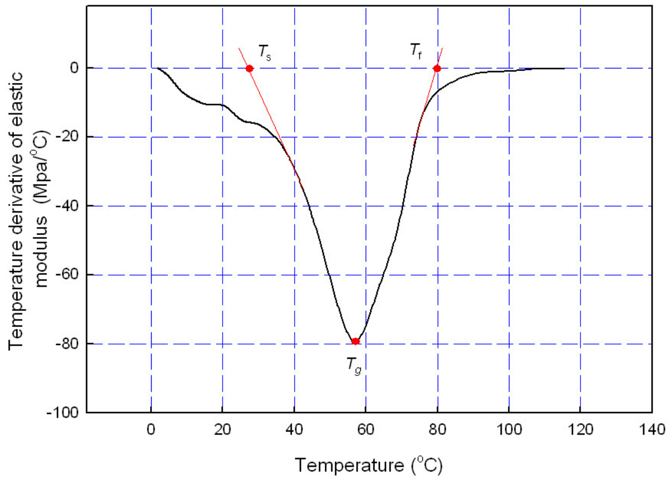

Fig. 2. Temperature derivative of elastic modulus-temperature curves of SMPC.

In this paper, three glass transition critical temperatures are defined based on the relationship of the temperature derivative of elastic modulus and temperature, shown in Fig 2. They are glass transition starting temperature, T_s, glass transition temperature, T_g, and glass transition finishing temperature, T_f. The elastic moduli corresponding with T_s, T_g and T_f are respectively expressed as E_s, E_g and E_f and their values can be found in Fig. 1. The values of glass transition critical temperatures and their corresponding elastic moduli of SMPC and SMP are listed in Table 1.

Table 1. Values of glass transition critical temperatures and corresponding elastic moduli.

	T_s/°C	T_g/°C	T_f/°C	E_s/Mpa	E_g/Mpa	E_f/Mpa
SMPC	27	57	80	2560	1200	372
SMP	42	57	68	1520	700	337

5. Glass Transition Model

During the process of glass transition, the material temperature increases from glass transition starting temperature, T_s, to glass transition finishing temperature T_f. The relationship between temperature derivative of elastic modulus and temperature should be expresses by the curve segment of '$T_sT_gT_f$' in Fig. 2. Note that there are fluctuations in the curves of temperature derivative of elastic versus temperature, shown in Fig. 2, when temperature is below T_s. This is because that the heating is not uniform at the beginning of DMA test, so it is reasonable to use the curve segment of '$T_sT_gT_f$', shown in Fig. 2, to express the relationship between temperature derivative of elastic modulus and temperature.

The curve segment '$T_sT_gT_f$', shown in Fig. 2, can be formulated by

$$\begin{cases} \dfrac{dE}{dT} = a_1 \sin(\dfrac{\pi}{2}\dfrac{T-T_s}{T_g-T_s}) & (T_s \le T \le T_g) \\ \dfrac{dE}{dT} = a_2 \sin(\dfrac{\pi}{2}\dfrac{T-T_f}{T_g-T_f}) & (T_g \le T \le T_f) \end{cases} \tag{1}$$

Integral calculations on Eq. (1) leads to

$$\begin{cases} E = b_1 \cos(\dfrac{\pi}{2}\dfrac{T-T_s}{T_g-T_s}) + c_1 & (T_s \le T \le T_g) \\ E = b_2 \cos(\dfrac{\pi}{2}\dfrac{T-T_f}{T_g-T_f}) + c_2 & (T_g \le T \le T_f) \end{cases} \tag{2}$$

where b_1, b_2, c_1 and c_2 are integral constants. Using the boundary conditions of $E(T_g)=E_g$, $E(T_s)=E_s$ and $E(T_f)=E_f$, we can have $c_1=c_2=E_g$, $b_1=E_s-E_g$ and $b_2=E_f-E_g$. Substituting the values of b_1, b_2, c_1 and c_2 into Eq. (2) leads to the glass transition model, expressed as

$$\begin{cases} E = (E_s - E_g)\cos(\dfrac{\pi}{2}\dfrac{T-T_s}{T_g-T_s}) + E_g & (T_s \le T \le T_g) \\ E = (E_f - E_g)\cos(\dfrac{\pi}{2}\dfrac{T-T_f}{T_g-T_f}) + E_g & (T_g \le T \le T_f) \end{cases} \tag{3}$$

The glass transition model, Eq. (3), is used to predict the glass transition processes of SMP and SMPC. The material constants used in numerical calculations are listed in Table 1. Figure 3 shows the curves of elastic modulus versus temperature of SMPC described by the model and DMA test. The comparisons of elastic modulus-temperature curves from the model and DMA test reveal the glass transition model, Eq. (3), is able to predict the glass transition processes of SMPC or SMP effectively. The comparisons also explain the method of definition and determination on glass transition critical temperatures of SMP or SMP is reasonable.

6. Conclusions

DMA tests are operated on the styrene-based SMP and its carbon fiber fabric reinforced SMPC. Results show the reinforcement of SMPC improve the material stiffness when the temperature is below glass transition finishing temperature. A new method to determine the glass transition critical temperatures of SMP and SMPC is proposed and their material constants are determined according to this method. A new theoretical model describing the glass transition processes of SMPC or SMP is developed based on the DMA test. The comparison between numerical and experimental results illustrate the new glass transition model can well predict the glass transition behavior of SMPC or SMP.

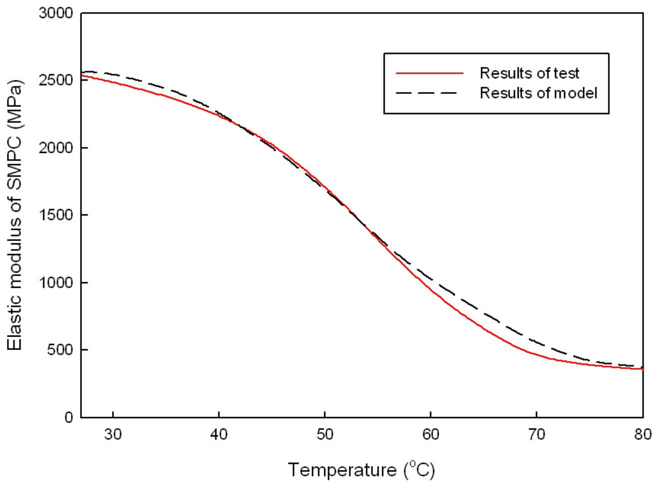

Fig. 3. Comparisons of Elastic modulus-temperature curves of SMPC by model and test.

Acknowledgments

The authors wish to acknowledge the supports provided by the National Science Foundation of China (Grant No. 95505010), National '863' Research and Development Plan of High Technology of China (Grant No. 2006AA03Z109) and China Postdoctoral Science Foundation (Grant No. 20080430933).

References

1. A. Bhattacharyya and H. Tobushi, *Poly. Eng. Sci.*, **40**, 2498 (2000).
2. F. E. Feninat, G. Laroche, M. Fiset and D. Mantovani, *Adv. Eng. Mater.*, **4**, 91 (2002).
3. S. Hayashi, *Inter. Prog. Urethanes*, **6**, 90 (1993).
4. K. Gall, M. L. Dunn, Y. Liu, D. Finch, M. Lake and N. A. Munshi, *Acta Mater.*, **50**, 5115 (2002).
5. M. C. Everhart, D. M. Nickerson, and R. D. Hreha, *Proc. of SPIE* **6171**, 61710K, (2006).
6. K. Gall, M. L. Dunn and Y. P. Liu, *Appl. Phy. Lett.*, **85**, 290 (2004).
7. B. Yang, W.M. Huang , C. Li, and L. Li, *Polymer,* **47**, 1348 (2006).
8. N. S. Goo, I. H. Paik, K. J. Yoon, Y. C. Jung and J. W. Cho, *Smart Stru. Integ. Sys.*, **5390**, 194 (2004).
9. T. Ohki and Q. Q. Ni, *Sci. Eng. Comp. Mater.*, **11**, 137 (2004).
10. T. Ohki, and Q. Q. Ni, *Composites*, **A35**, 1065 (2004).
11. K. Gall, M. Mikulas and N.A.Munshi, *J. Intell. Mater. Syst. Struct.*, **11**, 877 (2000).