Investigation on Structures and Properties of Shape Memory Polyurethane/Silica Nanocomposites

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In this study, high performance shape memory polyurethane (SMPU)/silica nanocomposites with different silica weight fraction including SMPU bulk, 3%, 4.5%, 6%, 7.5%, 10%, were prepared by sol-gel process initiated by the solid acid catalyst of *p*-toluenesulfonic acid (PTSA). Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) observation show that the silica nanoparticles are dispersed evenly in SMPU/silica nanocomposites. Tensile test and dynamic mechanical analysis (DMA) suggest that the mechanical properties and the glass transition temperature (T_g) of the nanocomposites were significantly influenced by silica weight fraction. Thermogravimetric analysis (TGA) was utilized to evaluate the thermal stability and determine the actual silica weight fraction. The TGA results indicate that the thermal stability can be enhanced with the hybridization of silica nanoparticles. Differential scanning calorimetry (DSC) was conducted to test the melting enthalpy (ΔH) and the results suggest that the ΔH was markedly improved for the SMPU/silica nanocomposites. Thermomechanical test was conducted to investigate the shape memory behavior and the results show that the shape fixity is improved by hybridization of silica and good shape recovery can be obtained with the increasing of cycle number for all the samples.

Keywords shape memory polyurethane, sol-gel process, solid acid, mechanical property, shape memory behavior

Introduction

Due to their thermally and electrically triggered shape memory characteristics, shape memory polymers (SMPs) are widely used in medical devices, textile industry, automobile, positive temperature coefficient (PTC) sensors, etc.¹⁻³ SMPs have the advantages such as light weight, large recoverability, lower cost and so on.^{4,5} Especially, shape memory polyurethane (SMPU) is the most extensively and specifically investigated SMPs presently for its flexible molecular design and its promising applications such as good permeability, damping and shock resistance based on its shape memory effect.⁶ Those characteristics result in promising applications of SMPU in various areas. However, the low stiffness, low thermal stability and low strength of SMPU restrain its further application. Thus, a lot of studies have been done to investigate the thermomechanical properties and shape memory effect of SMPU.

Fabrication of SMPU composites by incorporating reinforcements such as fibers and inorganic particles in SMPU matrix is the main approaches to improve the thermomechanical properties of SMPU nowadays. However, searching a preferable way to prepare SMPU composites with high performance is not an easy job. Ni *et al.*⁷ reported that carbon nanotubes can efficiently increase the tensile strength and Young's modulus of

SMPU, however, the high cost of carbon nanotube and the nontransparency of the composites restrained its further application. It is reported by Liang *et al.*⁸ that glass fiber reinforced SMPU possesses increased strength, Young's modulus, and, however, decreased recoverable strain. Zhou et al.9 found that the mechanical properties of acrylic-based polyurethane could be enhanced via addition of nano-silica, while the glass transition temperature (T_g) was decreased. Meanwhile, the change of the coefficient of thermal expansion around T_g of SMPU is obvious.³ Moreover, the thermal expansion coefficient of SMPU matrix and its reinforcing fiber is usually different, which may lead to inferior interface combination under high temperature. Nano-particles, due to their small size and high surface energy, exhibit high combination potentiality with polymer substrate, which is beneficial for the increase of the mechanical properties of the polymer.¹⁰ Nanosilica reinforced nanocomposites usually exhibit good interface interaction between polymer matrix and silica nanoparticles even under high temperature. Presently, there are just few researches on the application of silica in SMPU,^{11,12} as a consequence, nanosilica was chosen as the reinforcing material to functionalize SMPU in this study.

In this study, SMPU/silica nanocomposites were prepared with different silica weight fraction via a

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sol-gel process. Furthermore, the influence of silica weight fraction on the thermomechanical properties and shape memory behavior were investigated.

Experimental

Materials

The liquid shape memory polyurethane (Diary, MS-4510) was supplied by Diaplex Co., Ltd. of Japan. The weight ratio of SMPU to DMF is set to be $3 \div 7$. Tetraethoxysilane (TEOS), *N*,*N*-dimethylformamide (DMF), *p*-toluenesulfonic acid (PTSA) and absolute ethanol (EtOH) were all commercial products and used as received.

Preparation of SMPU/silica nanocomposites

As is known to us all, the material prepared by sol-gel process is easy to craze during drying, and it is difficult to obtain nanoparticles without aggregation.¹³ In the traditional sol-gel system, most of the catalyst reported was liquid acid,¹⁴⁻¹⁶ and the hydrolysis reaction was initiated by the addition of water directly. In the present investigations, the solid acid catalyst PTSA was employed and the hydrolysis reaction was initiated by the water in air instead of addition of water, aiming to obtain moderate hydrolysis reaction rate to avoid the cracking phenomena and the aggregation of silica. In this experiment, the mole ratios of PTSA and absolute ethanol to TEOS were about 0.05 and 4, respectively. The theoretical weight fraction of silica is used to classify the samples. The specific recipe is listed in Table 1 and the procedure is described as follows.

 Table 1
 The recipe of preparation of SMPU/silica nanocomposites

Sample	0%	3%	4.5%	6%	7.5%	10%
TEOS/g	0	1	1.5	2	2.5	3.5
SMPU/g	30	30	30	30	30	30
DMF/g	10	10	10	10	10	10
H_2O/g	0	air	air	air	air	air
PTSA/g	0	0.04	0.06	0.08	0.1	0.15
EtOH/mL	0	1	1.6	2	2.5	4

A certain amount of PTSA was dissolved in DMF and then the mixture was added into SMPU, stirred for several minutes and then obtained the solution A. A certain amount of TEOS and absolute ethanol were mixed homogeneously, marked as B mixture. Then B mixture was added into solution A slowly, stirring by magnetic stirrer for 2 h and the transparent sol was obtained. The above mixture was poured into a Teflon container and sealed with tinfoil with several pores. Then it was placed at 20 °C for several days. The gelled sample was obtained and then dried at 40, 60, 80 and 130 °C gradually for several days. The SMPU/ silica nanocomposites with silica weight fraction of 3%, 4.5%, 6%, 7.5% and 10%, respectively, were prepared.

Characterizations

The morphologies of the specimens were observed using a field emission scanning electron microscopy (FE-SEM, ULTRA 55, ZEISS, Germany) and a transmission electron microscopy (TEM, JEM2100), respectively. The glass transition temperature (T_g) was determined via a DMA Q800 (TA Instrument, America) at frequency of 1 Hz and heating rate of 3 °C/min from 20 to 70 °C. Thermogravimetric analysis (TGA, Perkin-Elmer Pyris 1) was conducted with a heating rate of 20 °C/min under the nitrogen condition from 30 to 800 °C. Differential scanning calorimetry (DSC) was conducted with a heating rate of 10 °C/min from 40 to 200 °C. The mechanical properties of the hybrids were determined on a universal testing instrument (INSTRON-5543) according to ISO 527: 1993.

Thermomechanical cycle tests were conducted by a universal testing instrument (KES-G1, Japan) with a temperature controlled chamber to determine the shape memory properties of shape fixity and shape recovery. Figure 1 shows the scheme of the thermomechanical cycle test. The specimen was heated to 70 \degree C and kept for 10 min, then it was stretched to maximum strain ε_m with a tensile speed of 10 mm/min and kept for 10 min with load (Process 1). The specimen was cooled to the room temperature maintaining the strain ε_m (Process 2), and then kept for 10 min without loading and obtaining the strain ε_u (Process 3). Then the specimen was heated from room temperature to 70 °C again without loading and kept for 10 min, where the strain $\varepsilon_{\rm p}$ occurred (Process 4). The rate of shape fixity $R_f(N)$, total rate of shape recovery $R_{r.tol}(N)$ and rate of shape recovery $R_r(N)$ at cycle number N were calculated from the following Eqs. (1), (2) and (3), respectively:

$$R_{\rm f}(N) = \frac{\mathcal{E}_{\rm u}(N)}{\mathcal{E}_{\rm m}} \times 100\% \tag{1}$$

$$R_{\text{r.tol}}(N) = \frac{\varepsilon_{\text{m}} - \varepsilon_{\text{p}}(N)}{\varepsilon_{\text{m}}} \times 100\%$$
(2)

$$R_{\rm r}(N) = \frac{\varepsilon_{\rm m} - \varepsilon_{\rm p}(N)}{\varepsilon_{\rm m} - \varepsilon_{\rm p}(N-1)} \times 100\%$$
(3)

where $\varepsilon_{\rm m}$, $\varepsilon_{\rm u}(N)$ and $\varepsilon_{\rm p}(N)$ is the maximum strain, fixity strain and residual strain, respectively.

Results and discussion

Morphologies of SMPU/silica nanocomposites

SEM and TEM were employed to observe the dispersion and structure of the silica nanoparticles in the nanocomposites. The SEM images of the nanocompo-



Figure 1 Scheme of the thermomechanical cycle.

sites are presented in Figure 2. It is shown that the silica nanoparticles with diameter of about 20—50 nm were obtained and exhibited even dispersion in SMPU matrix for all samples, indicating that SMPU/silica nanocomposites were prepared. In addition, from Figure 2 it can be seen that the nanocomposites exhibited good inter-

face bonding which have not been reported previously, indicating an outstanding nanocomposite was synthesized via the present sol-gel process. From the TEM photos in Figure 3, it could be seen that the size of silica nanoparticles clearly coincided with that of silica nanoparticles shown in SEM images. The SEM and TEM observation suggests that a novel SMPU/silica nanocomposite material was prepared in the present investigations, which could provide useful information to the sol-gel technology and preparation of hybrids via sol-gel process.

Thermal analysis of nanocomposites

Analysis of dynamic mechanical property

The relationships between tan δ and temperature for all the samples are shown in Figure 4. From the Figure 4, one can see that the T_g gradually increases from around 41 to 50 °C with the increase of silica weight fraction, which is attributed to the restrictions of silica nanoparticles on the molecular motions of PU chains. However, the incorporation of excess of silica such as 10% led to a decrease of T_g which was probably due to that the



Figure 2 SEM images of the cross-section surface of SMPU/silica nanocomposites: (a) SMPU bulk, (b) 3% silica, (c) 4.5% silica, (d) 6% silica, (e) 7.5% silica, (f) 10% silica.



Figure 3 TEM images of SMPU/silica nanocomposites: (a) 3% silica, (b) 6% silica, (c) 10% silica, (b1) and (c1) the larger scale of TEM for (b) and (c), respectively.



Figure 4 The change of tan δ with various silica weight fraction for SMPU/silica nanocomposites.

excess silica can increase the free volume in SMPU/silica nanocomposite. Though the T_g of the nanocomposite with 10% silica is lower than that of other silica weight fractions, it is still higher than that of pristine SMPU. Moreover, all the values of tan δ become higher except that of the nanocomposite with 10% silica, indicating the improved damping property of the

nanocomposites. The increase of the values of tan δ also indicates that the silica dispersed in the matrix evenly and the nanocomposites possess superior interface bonding. The storage modulus of the nanocomposites is shown in Figure 5. The value of the storage modulus around T_{g} varies remarkably and increases with the increase of silica weight fraction except for that of the nanocomposites with 10% silica, resulting from the reinforcement of silica nanoparticles. The reasons for the decrease in the storage modulus for the sample containing 10% silica could be considered as that it benefits to enhance modulus of composites with the increase of silica content, however, firstly, the size of particle tends to increase with the increase of silica content as seen from Figure 3 (b1) and (c1). The size of particle of composite with 10% silica is obviously larger than that of 6%, which will weaken the enhancement effect of silica. Secondly, the probability of particles entering into the hard segment of SMPU increases with the increase of silica content. The change of the value of storage modulus indicates that the material is easily deformed at high temperatures and also the deformation resistance is large at low temperatures, corresponding to the principle of shape memory behavior deformed at



Figure 5 The change of storage modulus with various silica weight fraction for SMPU/silica nanocomposites.

high temperature above T_g and frozen below T_g . The increase of the modulus also indicates the improvements of mechanical properties at room temperature.

TGA analysis of the nanocomposites

TGA curves for the pristine SMPU and the SMPU/silica nanocomposites are shown in Figure 6. All samples exhibit two thermal decomposition stages, which should be attributed to the decomposition of soft segment and hard segment of SMPU, respectively.¹⁷ From the figure it can be seen that the onset temperatures for all the SMPU/silica nanocomposites are almost around 307 °C, which are slightly higher than that of pristine SMPU. The onset temperatures at the second stage for all the SMPU/silica nanocomposites are around 396 $^{\circ}$ C, which are 11 $^{\circ}$ C higher compared with that of pristine SMPU. Consequently, it can be concluded that the addition of silica improve the thermal stability of the material, which possibly resulted from the even dispersion and good interfacial adhesion between silica and matrix. In addition, as can be seen in Figure 6, the residual ash weight fractions for SMPU/ silica nanocomposites measured at 750 °C roughly correspond to the theoretical values of silica synthesized



Figure 6 TGA curves of SMPU/silica nanocomposites with different silica weight fractions.

via sol-gel process in this study.

DSC analysis of the nanocomposites

The DSC curves for the pristine SMPU and the SMPU/silica nanocomposites are shown in Figure 7. The melting temperatures (T_m) and the melting enthalpys (ΔH) for all samples are listed in Table 2. The ΔH is calculated as follows:

 $\Delta H = \Delta H_0$ /actual amount of SMPU

where ΔH_0 is the enthalpy measured directly by the instrument.



Figure 7 DSC curves of SMPU/silica nanocomposites with different silica weight fractions.

Table 2 $T_{\rm m}$ and ΔH for all samples

	Pure	3.0%	4.5%	6.0%	7.5%	10%
$T_{\rm m}/{}^{\circ}{\rm C}$	146.2	141.0	143.6	142.7	143.1	142.2
$\Delta H/(\mathbf{J} \cdot \mathbf{g}^{-1})$	3.87	7.01	7.40	7.32	7.93	7.24

From the table it can be seen that the value of ΔH increases with the addition of silica remarkably. However, the weight fraction of silica shows little effect on the value of ΔH . The above results suggest that the silica nanoparticles act as nucleating agent and increase the crystallinity of the soft segment of SMPU. Nevertheless, with the increase of silica weight fraction, the growth of the crystalline will be restrained, resulting in the decrease of the integrity and the size of crystalline, which may lead to the melting peak moving to the low temperature slightly.

Static tensile mechanical property

The stress-strain curves for the nanocomposites with different silica weight fraction and pristine SMPU are shown in Figure 8. The yielding phenomenon was observed in all samples with different silica weight fraction. The samples of pristine SMPU, nanocomposites with 3%, 4.5% and 6% silica did not rupture within the strain of 300% showing excellent toughness. However, the nanocomposites with 7.5% and 10% silica showed inferior fracture strains of 190% and 250%, respec-



Figure 8 Stress-strain curves for all samples.

tively. It is believed that the incorporation of excess silica hindered the motions of chains and the propagation of cracks occurred more easily, leading to lower fracture strain for nanocomposites with 7.5%, 10% silica. In addition, it can be seen that the tensile stress become much larger for SMPU/silica nanocomposites than that of pristine SMPU within the strain of 300%, and the nanocomposite with 6% silica weight fraction exhibits maximum stress. The enhancement of stress probably results from the fine dispersion and the strong interfacial interaction generated between silica nanoparticles and SMPU matrix. The relationships between the Young's modulus and silica weight fraction are shown in Figure 9. The Young's modulus was calculated by linear region within the strain of 0.2% depicted in the small picture of Figure 8. Compared with the pristine SMPU, there is an increment of 587%, 612%, 631%, 670% and 562% for the Young's modulus of the nanocomposite with 3%, 4.5%, 6%, 7.5% and 10% silica weight fraction, respectively. This increment of Young's modulus is also attributed to the block of the motion of SMPU chains resulted from strong interfacial bonding between evenly dispersed



Figure 9 Relationships between Young's modulus and silica weight fraction for all samples.



Figure 10 Stress-strain curves in the thermomechanical cycle tests for four materials: SMPU bulk, 3%, 6%, 10% silica, respectively.

silica and the matrix. The reasons for the decrease in Young's modulus for the sample containing 10% silica could be considered as well as that of the storage modulus.

Shape memory properties

The stress-strain curves obtained in the thermomechanical cycle test of the maximum strain of $\varepsilon_m = 50\%$ for samples with 0, 3%, 6% and 10% silica are shown in Figure 10. As shown in the figure, the value of stress for each nanocomposite is bigger than that of pure SMPU, and the maximum stress increased with increase of the cycle number *N* which possibly resulted from the orientation of molecule chains, indicating that the materials possess increased shape recovery force. The maximum stress has not significant change after the second cycle for all samples.

The shape fixity and shape recovery properties of pristine SMPU and SMPU/silica nanocomposites determined from the results of thermomechanical cycle tests as above are shown in Figure 11. The values of the shape fixity ratio and shape recovery ratio are defined by Eqs. (1), (2) and (3), respectively.

As seen in Figure 11(a), the ratio of shape fixity (R_f) is almost constant and independent of N for each sample. This resulted from the fact that the modulus of elasticity is large at room temperature and does not change under cycling. The R_f for each nanocomposite can almost maintain at 90%, while that is 85% for pristine SMPU. It is obviously that the developed nanocomposites show better shape fixity property than that of pure SMPU.

As seen in Figure 11(b), the ratio of total shape recovery $(R_{r.tol})$ roughly decreased with the increase of silica weight fraction and cycle number, however, the $R_{\rm r.tol}$ will not change much after the second cycle for each specimen. The decrement of $R_{r,tol}$ with the increase of cycle number is expected to the loss of energy correlated with the stress relaxation in the process 2. In the process of maintaining strain, the stress relaxation occurs. Consequently, the stress decreases and ultimately approaches a certain constant value due to the frozen of the SMPU chains in process 3. After the second cycle, the effect of stress relaxation is not significant, thus, a stable $R_{r.tol}$ can be obtained after several cycles. In addition, it seems that the reduction of $R_{r,tol}$ of SMPU/silica nanocomposites is lower than that of pure SMPU, indicating that the silica nanoparticles can decrease the coefficient of stress relaxation of SMPU matrix effectively after the second cycle.

As seen in Figure 11(c), the ratio of shape recovery $[R_r(N)]$ is about 85%—95% when N=1, and increases with increase of cycle number for each specimen. The $R_r(N)$ nearly equals to 100% when N>3. It is believed that the reasons for this result is attributed to the failure propagated hardly in the developed nanocomposites due to the resistance of silica⁴ and a constant stress could be obtained after several cycles. It indicates excellent shape



Figure 11 Relationships between shape memory properties and cycle numbers for all samples: (a) shape fixity, (b) total shape recovery, (c) shape recovery.

recoverability can be obtained for the materials after several cycles, which is called training effect as reported by Tobushi *et al.*¹⁸

Conclusions

In the present investigations, shape memory polyurethane/silica nanocomposites with different silica weight fraction were prepared via sol-gel process using the catalyst of solid acid PTSA. The structure, thermomechanical properties and shape memory properties

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of the nanocomposites were investigated. The results obtained are remarked as follows.

(1) SMPU/silica nanocomposites with even dispersion of silica were prepared. The morphology investigation of the nanocomposites indicated that the diameter of silica nanoparticle was around 20—50 nm and the nanocomposite exhibited good interface interaction.

(2) The glass transition temperature (T_g) increases with the increase of silica weight fraction, however, excess silica weight fraction will decrease the T_g , which is still higher than that of pristine material. The thermal stability and the melting enthalpy (ΔH) were improved with the hybridization of silica.

(3) The Young's modulus and tensile stress markedly enhanced with the addition of silica nanoparticles, and it seems existing an optimum silica weight fraction around 6%.

(4) The ratio of shape fixity of the SMPU/silica nanocomposites is much better than that of pure SMPU. A constant outstanding ratio of shape recovery almost equal to 100% can be obtained after several cycles.

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