



Analyzing effects of interfaces on recovery rates of shape memory composites from the perspective of molecular motions

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ABSTRACT

Over recent years, researchers have noticed that recovery rates of shape memory composites (SMCs) would vary due to the addition of fillers. So far, although several superficial reasons are discussed, a thorough analysis has not been presented yet probably due to the absence of a microscopic mechanism of SMCs. Here, a molecular mechanism of SMCs is clarified by identifying the differences lying in molecular motions of shape memory polymers and SMCs. On the basis of the molecular mechanism of SMCs, both a positive effect and a negative effect of fillers on recovery rates are revealed. Because interfaces between fillers and matrices play a decisive role in the two effects of fillers, several experiments are designed to verify the role of interfaces. The experimental results prove that the interfaces are benefit and harmful for recovery rates at the same time. Moreover, the results are able to qualitatively predict that the recovery rates of SMCs would increase or decrease with more addition of fillers.

1. Introduction

Since the heat shrinkable ability of polyethylene was discovered in 1960s [1], shape memory polymers (SMPs) have attracted many researchers because of the light weight, easy processing, low costs and large deformation [2,3]. For advanced material performances, shape memory composites (SMCs) are developed on the basis of a combination of SMPs and fillers. Several kinds of fillers are employed to enhance the elastic moduli and recovery stresses [4,5], endow SMCs with the electroactive actuation [6–10] and remote activation [11,12], improve the self-healing property [13] and heighten shape memory performances with induced co-continuous structures [14]. Though most of researchers focus on their desired performances, the changes in recovery rates of SMCs are still reported. Not only the decreases in recovery rates are found [4,5,15,16], but also the increases in recovery rates are discovered [17,18]. Some researchers respectively give simple reasons according to their own work, but the given reasons contradict others' work (detailed discussion on the reported reasons is in Appendix A). In fact, compared with the experimental researches on SMCs, theoretical analyses are very few. Two models for evaluating interfacial adhesion are introduced to attempt to find out a relationship between shape memory properties and interfacial bonding [19], but the conclusion is only based on SMCs with low percents of fillers. A bridging

model is applied to predict recovery performances [20], whereas the predictions are just simulation without comparisons with recovery experimental data.

So far, a thorough analysis on the variations in recovery rates induced by fillers has not been presented yet, maybe because the molecular mechanism of SMCs is unclear. It is unlike the molecular mechanism of SMPs which has been discussed schematically [21–23]. Another possible reason may be that the mechanism of SMCs is considered to be the same as that of SMPs (reference 18). As we know, a microscopic mechanism would be greatly helpful to understand material behaviors essentially and explore expected properties for promising applications. Moreover, with the rapid development in recent years [24], the molecular mechanism of SMCs become more and more important.

In this study, the molecular mechanism of SMCs is clarified by analyzing the distinctions between molecular motions of SMPs and SMCs. According to the molecular mechanism of SMCs, interfaces between fillers and matrices are the essential reason for variations in recovery rates of SMCs and effects of the interfaces on recovery rates are both positive and negative. To clarify the role of interfaces in shape recovery behaviors, two kinds of fillers are selected to synthesize SMCs and several experiments are designed. Comprehensive conclusions based on the experimental results can supply a general explanation for

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the variations in recovery rates of reported SMCs and qualitative predictions for the trend of changes in recovery rates.

2. Materials and methods

2.1. Hot-pressed lead zirconate titanate (PZT)/SMP composites

PZT/SMP composites were synthesized by PZT particles (DPZ-LQ2-P6, Dai Nippon Toryo Co., Ltd., Japan) and a kind of commercial shape memory polyurethane (MM6520, SMP Technologies Inc., Japan). First, PZT particles, with the average equivalent diameter of 400 nm and density of 7.9 g/cm³, were poured into tetrahydrofuran (THF) and an ultrasonic device (Sonifier 250, Branson Ultrasonics Corp., U.S.A.) was employed to disperse PZT particles for 15 min at the level 3. After dispersion, shape memory polyurethane pellets (the weight was one seventh of THF), with the glass transition of 65 °C and density of 1.25 g/cm³, were dissolved in the PZT/THF suspension and the mixture was stirred magnetically for 48 h at a speed of 400 r/min. Then THF evaporated naturally when the mixture was still stirred until the weight ratio of shape memory polyurethane and THF became 1:5. After the mixture was put statically for 48 h to remove air bubbles, it was casted on a teflon film with an auto film applicator (PI-1210, Tester Sangyo Co., Ltd., Japan). The resulting films cured after evaporating THF again for 3 days in nature. The obtained PZT/SMPU composite films were further dried at 65 °C for 3 days and then pressed for 8 h under the pressure of 6 MPa at 80 °C by a hot-press machine (SA-303, Tester Sangyo Co., Ltd., Japan).

2.2. Hot-pressed TiO₂/SMP composites

TiO₂/SMP composites were synthesized by TiO₂ whiskers (FT-3000, Ishihara Sangyo Kaisha, Ltd., Japan) and the same shape memory polyurethane. The average diameter, the average length, the density of TiO₂ whiskers are respectively 270 nm, 5.15 μm and 4.3 g/cm³. The synthetic procedures were the same as those of hot-pressed PZT/SMP composites.

2.3. Pristine SMP films

Pristine SMP films were prepared in the same methods without the addition of fillers and the dispersion of fillers.

2.4. PZT/SMP and TiO₂/SMP composites without hot-pressing

This group of materials were compounded in the same methods except the hot-pressing.

2.5. Recovery rate tests in three cycles

The shape memory recovery rates of PZT/SMP composites and TiO₂/SMP composites were all measured by a thermo-mechanical analyzer (TMA/SS6100, Hitachi High-Tech Science Corp., Japan). Rectangle samples with the width of 2 mm, length of 10 mm and thickness between 127 and 150 μm were tested for 3 cycles in the controlled force mode. To insure all samples were measured under the same stress state, the applied force for every sample was calculated in advance. Before the cyclic tests, the samples were heated from ambient temperature up to 71 °C with a stress of 0.025 MPa to protect samples from buckling. The maximum loaded stress in these tests was 3.5 MPa to ensure that the stretched length of the pristine SMP must be in the measuring range of TMA/SS6100. One experimental cycle was that

firstly the stress was increased to 3.5 MPa at a speed of 0.139 MPa/min, then a fan was employed to quickly cool the samples down with the stress of 3.5 MPa, next the stress was unloaded from 3.5 to 0.025 MPa at a speed of - 0.695 MPa/min and finally the samples were heated up to 71 °C again while the stress was kept at 0.025 MPa. The strain of every sample was the quotient of the continuous displacement recorded by TMA device and its length.

2.6. Field emission scanning electron microscopy (FE-SEM)

The microscopic images of interfaces between fillers and SMP matrices were taken by a field emission scanning electron microscopy (S-5000, HITACHI CO., LTD., Japan). The images were all from cryo-fractured surfaces.

3. Molecular mechanism of shape memory composites

At present, the molecular mechanism of SMPs generally accepted is described as following [21–23]. The chain segments (soft segments) between netpoints (hard segments which determine the permanent shapes) could deform quite freely at temperature above the thermal transition temperature (T_{trans}). The deformation of chain segments would store strain energy. If temperature is below T_{trans} , the deformation of chain segments would be freezing or at least partly constrained by vitrification, crystallization, or other means [25]. When temperature goes above T_{trans} again, the chain segments would be liberated and recover to their original shapes by releasing the stored strain energy. The recovery force is entropic force from changes in conformational entropy.

On the basis of the above mechanism, two obvious phenomena, which don't exist in the molecular motions of SMPs, are presented by taking the fillers into consideration:

- (1) The movements and deformation of the chain segments in the interfaces are the same as that of fillers, if the interfaces are not damaged (the chain segments in the interfaces means the chain segments forming interfacial bonding).
- (2) The deformation of the chain segments out of the interfaces is much greater than that of the chain segments in the interfaces at temperature above T_{trans} .

The first difference is easily understandable, because, if it is untrue, fillers and the chain segments in the interfaces would be apart (in other words, the interfaces would be broken). The second difference results from the fact that the chain segments out of the interfaces could easily generate large strains due to the chain mobility at temperature above T_{trans} [26] but the chain segments in the interfaces almost keep their initial shapes because of the first difference and the almost ignorable deformation of fillers (most of the fillers added in SMPs are usually much harder than the chain segments at temperature above T_{trans}).

According to the above two differences, the molecular mechanism of SMCs is clarified (Fig. 1). When temperature is above T_{trans} , the chain segments out of the interfaces (blue full lines in Fig. 1) could freely deform but the deformation of fillers and the chain segments in the interfaces (red dashed lines in Fig. 1) would be very few. All the deformation would store strain energy. Besides, fillers would move with the chain segments. If temperature falls below T_{trans} , all the deformation would be frozen or at least partly constrained by different means. When temperature goes above T_{trans} again, the chain segments out of the interfaces would regain the chain mobility to recover to their original shapes naturally by entropic force. With the movements of the

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