

Internal stress storage in shape memory polymer nanocomposites

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We examine the storage and release of internal stresses in shape memory polymers reinforced with a dispersion of nanometer-scale SiC particles. A quantitative Rietveld analysis of diffraction peaks was used to measure changes in the lattice parameter of the SiC particles after permanent deformation at 25 °C, and subsequent shape recovery induced by heating to 120 °C. Under 50% compression of the composite material, the nanoparticles store a finite compressive stress, which is almost completely released during heated strain recovery. The values of the stored internal stresses in the particles are compared to values based on micromechanic calculations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1769087]

Shape memory polymers possess the capacity to recover large strains on the order of 50%–400% by the application of heat. The ability of shape memory polymers to spontaneously recover large strains in restricted environments has been exploited in numerous applications, such as heat-shrink tubing,¹ deployable aerospace structures,² microsystems,³ and biomedical devices.⁴ Although the recoverable strain limits in shape memory polymers are orders of magnitude higher than shape memory alloys or piezoelectric materials, their ability to generate a “recovery” stress under strain constraint is limited by their relatively lower stiffness. However, the stiffness and recovery stress of shape memory polymers can be substantially increased, at the expense of recoverable strain, by the inclusion of hard ceramic reinforcements.³ In the present study, we examine the storage and release of internal stress in nanometer-scale SiC ceramic reinforcements embedded in an amorphous active shape memory polymer matrix. Although the shape memory effect is not inherent to the ceramic nanoparticles, the present results demonstrate that elastic strain is stored in the nanoparticles during deformation, and released during subsequent heating.

The thermomechanical response of shape memory polymers is defined by four critical temperatures. The glass transition temperature T_g is the reference point for thermomechanical deformation and recovery. The deformation temperature T_d is the temperature at which the polymer is deformed into a temporary shape. The initial deformation at T_d can occur above or well below T_g , depending on the desired recovery response.³ The storage temperature T_s is less than or equal to T_d and constitutes the temperature at which the temporary shape is stable over time. After deformation at T_d , the material is typically cooled to T_s with varying degrees of strain/stress constraint, ranging from no constraint to full constraint. In some instances, such as in the present study, T_d is equal to T_s , and cooling is not necessary after deformation, analogous to the shape memory effect in metals. The recovery temperature, T_r , represents the temperature at which the material recovers its original shape during heating. Recovery can be accomplished isothermally by heating to a fixed T_r

and then holding, or by continued heating, up to and past T_r .

Shape memory polymer composite samples were prepared by mixing 20 wt % SiC nanoparticles, with an average diameter of 700 nm, into a two-part epoxy shape memory polymer resin. The particles were well dispersed as confirmed with scanning electron microscopy.³ The samples were cured in a Teflon mold and sliced into samples for compression testing and x-ray diffraction (XRD) measurements. The glass transition temperature T_g of the nanocomposite materials, defined by the peak in Tan Delta, was measured to be $T_g=100$ °C. The initial drop in storage and loss modulus of the nanocomposite occurred at a temperature near 80 °C. Numerous samples were compressed to an approximate true strain of 50% at a temperature of $T_d=25$ °C. Several of the compressed samples were recovered by heating up to a temperature of 120 °C under both free- or fixed-strain boundary conditions. XRD measurements were made with Cu K radiation collimated with Soller slits and a 2 mm divergence slit, and data were collected using Ge solid-state detector. In order to obtain better statistics, XRD patterns of each sample were collected in three separate scans with steps of 0.02° in 2θ , θ defined as the Bragg angle, as follows: 25°–85° in 2θ , with a fixed counting time of 50 s/step, 85°–115° in 2θ , 100 s/step, 115°–140° in 2θ , 100 s/step.

Figure 1 presents the true compressive stress-strain response of the nanocomposite material at $T_d=25$ °C. The three insets in Fig. 1 are pictures of the nanocomposite sample (1) as prepared, (2) after compression, and (3) after heated shape recovery. The material exhibits an elastic response up to approximately 50 MPa followed by yield and inelastic flow up to 50% strain. Upon unloading, the material initially deforms elastically, followed by spontaneous strain recovery, indicated by the nonlinearity at lower stress levels. The residual inelastic strain after complete unloading is approximately 35%. Heating the material to $T_r=120$ °C induces full shape recovery of the nanocomposite. A duplicate sample in deformed state (2) was held under a fixed strain and subjected to the same heating profile that resulted in the full strain recovery and state (3). During heating, the sample attempts to expand against the fixed strain boundary condition, resulting in the generation of stress (Fig. 2). The gen-

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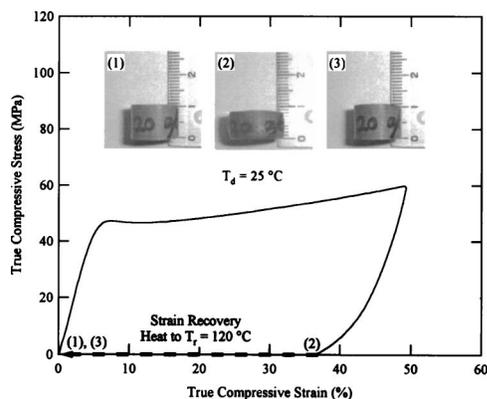


FIG. 1. The true compressive stress-strain curve and recovery response of the nanocomposite shape memory polymer. The insets show the sample shape (1) as processed, (2) after compression, and (3) after recovery. During heated strain recovery, the sample was free from applied boundary conditions.

erated stress peaks out near 80 °C, a temperature at which the composite modulus begins to drop, and the generation of recovery stress is circumvented by material softening. The overall stress generated in Fig. 2 is higher than can be generated with the pure shape memory polymer resin. The final compressive stress generated by the sample is governed by the modulus of the material at the highest temperature, 120 °C. To generate larger stresses, the material would need to be heated and held at a fixed temperature below 80 °C.

Duplicate samples in states (1), (2), and (3) from Fig. 1 were subjected to XRD measurements to be analyzed by the Rietveld refinement⁵ program GSAS⁶ (Fig. 3). XRD patterns indicate that the SiC nanoparticle crystal structure is hexagonal (6H polymorph). The shape memory polymer epoxy matrix is an amorphous, cross-linked polymer network. Using this analysis, both crystal structure and microstructure (texture, diffraction-line broadening effects, etc.) can be assessed. The SiC crystallites were approximately randomly distributed, and uniaxial compression did not introduce significant texture evolution. The refined values of the diffraction-line profile coefficients indicate anisotropic size and strain broadening with significantly larger values of both crystallite domain size and strain in the [001] direction, compared to the perpendicular directions. This is attributed to the

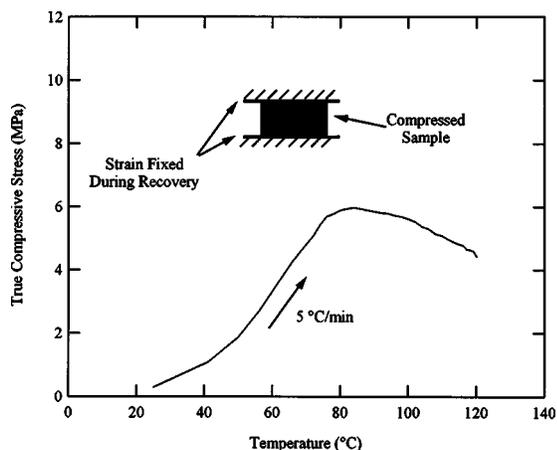


FIG. 2. The Evolution of the generated compressive stress as a function of temperature during a heating. The compressed sample was kept at a fixed strain during the heating process.

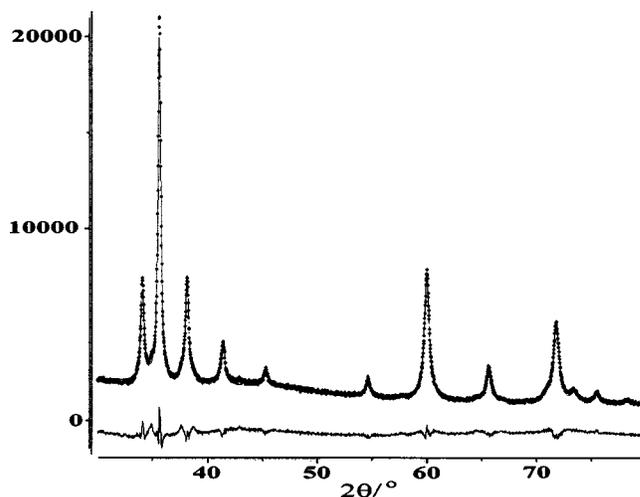


FIG. 3. The Rietveld refinement of the XRD pattern of the compressed nanocomposite sample. Symbols denote the measurements, the full lines are the calculated and background patterns, and the difference between the observed and calculated patterns is shown below.

rodlike shape of the crystallites of hexagonal SiC, which is elastically anisotropic.⁷ However, because of randomly dispersed SiC crystallites under uniaxial compression, we base our analysis on the average changes of the unit-cell volume. Thus, an average macroscopic residual stress of the SiC reinforcement was calculated by using the following relation:

$$\sigma_{SiC} = B_{SiC} \Delta V / V, \tag{1}$$

where $B_{SiC} = 220.29$ GPa, representing the bulk modulus of SiC 6H.⁷ The results of the XRD studies are provided in the Table I for the three composite samples and the pure reinforcement.

A negative change in the lattice parameters of the SiC reinforcement after incorporation into the composite indicates the introduction of a residual thermal compressive stress. This “processing” stress is caused by both shrinkage of the polymer matrix during curing, and thermal expansion mismatch upon cooling from the curing temperature. The compressed sample demonstrates a further decrease in the unit-cell volume from internal stresses in the particles created during the compressive loading. After recovery, the unit-cell volume of SiC increases toward the value in the as-processed composites, indicating the near-complete release of the stored stress in the particles.

In shape memory polymers, the relative motion and conformational rearrangement of long molecular chains is the primary inelastic strain mechanism. To maintain a deformed shape in a stable manner, new chain positions must be fixed by new bonds such as “switching” segments,⁸ bonds resulting from some type of crystallization,⁹ or physical entanglements. The development of the new bonds between molecular chains is typically a result of a temperature decrease and/or forced chain alignment. In the present material, compressing the sample past a critical stress induces relative chain slip, and creates a metastable structure. The metastable structure in the amorphous polymer likely contains both stored internal energy and increased chain organization (lower entropy). Upon unloading, the physical entanglements (temporary bonds) provide a storage mechanism for macroscopic stresses in the form of local internal stresses

TABLE I. The measured lattice parameters of SiC reinforcement in different states, and calculated values for σ_{SiC} .

Sample	a (Å)	c (Å)	$V(\text{Å}^3)$	$\Delta V/V$	σ_{SiC} (MPa)
Pure reinforcement	3.08165(12)	15.1162(7)	124.320(13)	0	0 ± 28.1
(1) As processed composite	3.08144(13)	15.1157(9)	124.299(18)	$-1.69e-4$	-37.9 ± 31.4
(2) Compressed composite	3.08127(13)	15.1148(8)	124.278(17)	$-3.38e-4$	-75.1 ± 30.7
(3) Recovered composite	3.08141(13)	15.1156(9)	124.295(18)	$-2.01e-4$	-43.6 ± 31.8

and a changed state of entropy. Upon subsequent heating, the bonds are weakened and the local internal stress field and low entropy state drive individual chains toward their initial positions, facilitating shape memory. The XRD measurements demonstrate that internal stress is also stored in the nanoparticulate reinforcements. Consequently, we conclude that the reinforcements contribute to the generation of external stress under constrained shape recovery by releasing stored elastic strain energy. The strain energy is stored by the constraining effect of the shape memory polymer matrix, which is frozen in a temporary shape by the transitory molecular interactions. The high relative stiffness of the nanoparticles results in an increase in the constrained recovery force, compared to a pure shape memory polymer material.

Finally, we use a micromechanic technique to estimate the internal hydrostatic stress generated in the SiC particles during the applied 50% strain. As expected, an elastic calculation, based on the Mori-Tanaka¹⁰ effective field theory greatly overestimates the stress, yielding a value of about 450 MPa. This is because at room temperature, the shape memory polymer itself exhibits elastic-plastic behavior, similar to Fig. 1. Incorporating the measured elastic-plastic stress-strain curve of the shape memory polymer,³ we

applied the micromechanics technique developed by Ref. 7, yielding a value of 43 MPa, in reasonable agreement with the measured change of internal stress during deformation and recovery of 31 MPa.

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