

Shape memory and nanostructure in poly(norbornyl-POSS) copolymers

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Abstract: The microstructure and shape-memory properties of norbornyl-POSS hybrid copolymers having either cyclohexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS) were investigated by transmission electron microscopy and thermomechanical analysis. Here, POSS refers to the polyhedral oligomeric silsesquioxane macromer. Samples containing 50wt% of POSS macromer have been mechanically drawn at temperatures above their glass transition temperatures, followed by rapid quenching in LN₂. Shape-memory properties of such drawn samples were explored by measuring recovered strain while heating above the T_g using thermomechanical analysis. Incorporation of POSS comonomers within PN is found to slightly reduce the percentage recovery, while improving thermal stability significantly. Interestingly, the types of corner groups in the POSS macromer affect the shape-memory behaviour, with the CyPOSS copolymer showing lower percentage recovery than the CpPOSS copolymer due to enhanced aggregation of CyPOSS macromers.

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INTRODUCTION

Shape memory refers to the ability of certain materials to remember a shape, on demand, even after rather severe deformations. The most common material exhibiting such a property is nitinol, a nickel–titanium alloy the shape-memory effect of which is produced by a solid-state phase transformation.¹ In recent years, shape-memory polymers have received increasing attention because of their low cost, low density, high shape recoverability and easy processability, compared to conventional shape-memory alloys.^{2–4} Basic principles of the shape-memory effect in polymeric materials can be well described by their elastic modulus–temperature behaviour. At temperatures above the glass transition temperature (T_g), the polymer achieves a rubbery elastic state where it can be easily deformed without stress relaxation by applying external forces over a time-frame $t \ll \tau$, where τ is a characteristic relaxation time. When the material is cooled below its T_g , the deformation is fixed and the deformed shape remains stable. The pre-deformation shape can be easily recovered by reheating the material to a temperature higher than the T_g . Therefore, admirable shape-memory behaviour requires a sharp transition from glassy state to rubbery state, a long relaxation time, and a high ratio of glassy modulus to rubbery modulus.

Several research groups^{5–11} have previously considered the shape-memory properties of polymers having two phases or showing crosslinked structure. Much of their research has concentrated on polyurethane-type shape-memory polymers,^{5–7,9,10} perhaps because of the high strain recovery (more than 95%), and the high degree of chemical control over the softening/retraction temperature (-30°C to 70°C), allowing a broad range of application. Besides the segmented polyurethanes, highly entangled polynorbornene has been reported to exhibit excellent shape recovery because of its long relaxation time (for temperatures slightly higher than T_g) and the convenient proximity of its T_g to room temperature ($T_g \approx 35\text{--}50^\circ\text{C}$).² Despite these desirable characteristics, polynorbornene exhibits relatively poor resistance to creep in the retracted state for ($T > T_g$), which limits its application at high temperature. In this study, we examine polynorbornene which has been reinforced with nanoscale inorganic molecules (POSS, described below) to improve stability against creep by creating a unique inorganic–organic hybrid polymer with enhanced mechanical properties and thermal stability while maintaining a desirable recoverable strain.

The polyhedral oligomeric silsesquioxane (POSS) macromer, consisting of a spherical inorganic silica

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core (Si_8O_{12}) surrounded by seven inert alkyl groups for solubility and one reactive group, is a well-defined cluster whose diameter is approximately 15 Å. The introduction of such nano-scaled POSS macromers into the organic polymer backbone by polymerization at the single reactive site (one of the eight corner groups in a POSS macromer) leads to increased T_g and T_{dec} , improved oxidation resistance, reduced flammability and mechanical reinforcement.^{12–16} Recently, we have successfully synthesized a series of random copolymers of norbornene/POSS–norbornene, and characterized their microstructure and mechanical relaxation behaviour.¹⁶ As anticipated, T_g increased with increasing POSS content in a manner similar to other POSS-based hybrids such as POSS–styryl^{12,15} or POSS–urethane¹³ copolymers. More interestingly, the microstructural ordering of POSS macromers in the norbornyl matrix (as manifested in wide-angle X-ray scattering data) was found to depend on the types of alkyl corner groups present in POSS macromers with the microstructure impacting the thermal and mechanical properties. Here we report our preliminary results on the shape-memory properties of polynorbornene homopolymer and norbornyl–POSS hybrid copolymers having either cyclohexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS). Our discussion will focus on how shape memory properties of the parent polymer (polynorbornene) can be affected by POSS macromers and the types of corner groups present in POSS macromers.

EXPERIMENTAL

For this study, we have examined polynorbornene homopolymer and random copolymers of norbornene/POSS–norbornene containing either 50 wt% CpPOSS–norbornyl monomer or 50 wt% CyPOSS–norbornyl monomer, which will be denoted hereafter as PN, 50CpPN, and 50CyPN, respectively. Synthesis details for the polymers under study have been reported previously and the interested reader is referred to ref.¹⁶ The number-average degrees of polymerization, measured using multiangle static light scattering together with gel chromatography (GPC) are approximately 381, 983 and 1337, for PN, 50CpPN and 50CyPN, respectively. Due to the POSS reinforcement, the glass transition temperature (mid-point in step-rise of heat capacity) of PN has been enhanced from 57 to 66.4 °C for 50CpPN and 73.2 °C for 50CyPN. We note that the glass transition is significantly broadened for the 50CyPN sample so that comparison of the T_g onset values yields close similarity for the POSS copolymers: 46.8 °C, 55.9 °C and 56.2 °C for PN, 50CpPN and 50CyPN, respectively. Shown in Fig 1 are the DSC traces for all three materials, including demarcation of the mid-point T_g values (vertical lines) and T_g onset values (circles).

Thin films for tensile drawing were obtained by solution casting. The solvent (*p*-xylene) was evaporated very slowly at room temperature for a period of

more than 5 days. Residual traces of solvent were removed at 60 °C under vacuum for an additional 3 days. The cast films were then cut into strips and fixed at their ends in a custom drawing apparatus. The sample dimensions were 0.25 mm thick, 2 mm wide and 15 mm long. The cast and cut films were stretched in a water bath at a constant draw rate (5 cm s^{-1}) and at temperature $T = T_g + 15$ °C to a tensile strain of 300% (4 × draw). We note that water uptake under these conditions was negligible for all the samples. Before stretching, the films were equilibrated at the drawing temperature for at least 1 min. In order to minimize stress relaxation, the stretched films were quenched in LN_2 immediately after drawing. Shape-memory properties of such drawn and quenched specimens were characterized by measuring recovered strain in a heating process of constant heating rate (4 °C/min) using a dynamic mechanical analyser (Perkin Elmer DMA-7) run in tensile mode with a fixed load.

RESULTS AND DISCUSSION

Figure 2 shows the percentage strain versus temperature for PN, 50CpPN and 50CpPN at an applied tensile stress of 0.8 MPa, where 300% strain corresponds to the drawn state and 0% strain corresponds to complete retraction to the original film dimensions. We first describe the response of PN homopolymer. In the low temperature region, the size of the specimen does not change significantly with temperature until $T > T_g$, at which point the retraction process begins. The initial retraction process, which is relatively slow, is followed by a sudden increase in the retraction rate with increasing temperature. Most of the recovery occurs over a narrow temperature range ($T_g < T < T_g + 10$ °C), where retraction occurs with a nearly constant rate of about 25% °C⁻¹ (100% min⁻¹). Above $T \approx 60$ °C the specimen approaches its maximum retraction, and further heating causes a redrawing of the specimen when the applied tensile stress exceeds the retractive stress. Finally, the specimen fails.

Incorporation of POSS comonomers within PN modifies shape-recovery properties significantly. As is seen by the dashed curves in Fig 2, the temperature for the onset of retraction is increased due to the increase in T_g , the temperature range for the recovery is broadened, and the retraction rate is slightly lower than PN. This is probably due to a hindrance of relaxation of PN chain orientation by the presence of POSS molecules and their aggregates (discussed below). Both POSS hybrid copolymers (50CpPN and 50CyPN) show nearly the same temperatures for the onset of strain recovery, which are close to the glass transition onset values for 50CyPN and 50CpPN, obtained using DSC. This result indicates that the initial recovery process begins near the temperature of the onset of glass transition. More importantly, we see in Fig 2 that POSS hybrid copolymers do not show significant redrawing behaviour at the applied stress

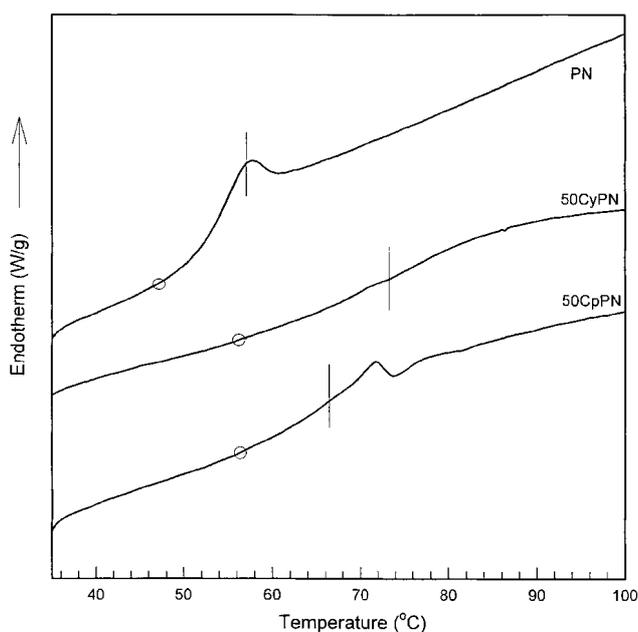


Figure 1. Differential scanning calorimetry (DSC) traces for PN (top), 50CyPN (middle), and 50CpPN (bottom). Vertical line demarcations indicated midpoint T_g values, while circle demarcations indicated the T_g onset values. Second heating data are used with a heating rate of $10^\circ\text{C}/\text{min}$ and a nitrogen atmosphere.

used, even at high temperature. This indicates a favourable reinforcement of the high temperature retracted state which we believe results from strong intermolecular POSS–POSS interactions.

We find that the percentage recovery achieved during retraction is a decreasing function of applied stress, as shown in Fig 3, for all three polymers. Additionally, the percentage recovery for given applied stress values is largest for PN, followed closely by 50CpPN, with 50CyPN showing the lowest values. In particular, the percentage recovery values for the case of no applied stress were 92% for PN, 84% for 50CpPN, and 70% for 50CyPN (see Fig 3), each polymer following a negative slope of approximately $14\% \text{MPa}^{-1}$. Surprisingly, little to no plateau in percentage recovery at low applied stress is observed (except for a slight plateau exhibited by 50CyPN) suggesting that, even at very low applied stresses, some amount of plastic draw competes with retraction. To understand the lowering of percentage recovery with POSS-copolymerization, particularly for 50CyPN, we have examined the sample morphology at the nanometer length-scale using transmission electron microscopy (TEM).

Transmission electron micrographs obtained from ultramicrotomed thin sections (about 60 nm thickness) of undrawn cast films of 50CyPN and 50CpPN (PN is featureless) are shown in Fig 4. Bright field images were obtained using combined mass-thickness and phase contrast with a 120 keV JEOL 1200EX transmission electron microscope. Because of the high electron density difference between PN and POSS molecules, enough contrast could be obtained without any chemical treatment, yielding images in which

POSS-rich phases appear as a dark phase, as a result of higher electron density. The TEM image of 50CyPN (Fig 4a) shows that the aggregation of CyPOSS molecules leads to the formation of short cylinders. Many spherically shaped domains can also be observed, resulting from cylinders which are cut perpendicular to their long axis. The average length and diameter of POSS-rich cylinders in 50CyPN are approximately 62.5 nm and 12 nm, respectively. Significantly, the size of POSS-rich domains are greatly decreased to about 36 nm in length and about 6 nm in diameter for 50CpPN (Fig 4b). These small dimensions with respect to the section thickness (about 60 nm) lead to relatively weak image contrast compared to 50CyPN, because more CpPOSS-rich domains were embedded within the sectioned film. It should be noted that neither 50CpPN nor 50CyPN forms POSS-rich domains with long-range order, which is also confirmed by small-angle X-ray scattering showing the absence of scattering features for angles as low as about $0.15^\circ 2\theta$ ($\sim 500 \text{ \AA}$ d -spacing).

If we assume that POSS cages occupy the whole of the POSS-rich domains, we can estimate the number of POSS cages in each POSS domain, based upon the distance between POSS cages (about 10.65 \AA) measured by WAXS.¹⁶ This estimation indicates that each CyPOSS domain contains seven times more POSS cages than each CpPOSS domain, supporting a proposed morphological characteristic derived from X-ray and DMA data in our previous report.¹⁶ We have suggested that there is a local exclusion of norbornyl segments due to the enhanced ordering of POSS cages in CpPN copolymers, which reduces the POSS–norbornene interaction volume and the impact of POSS on thermal and mechanical properties. Based on the size differences between CyPOSS-rich and

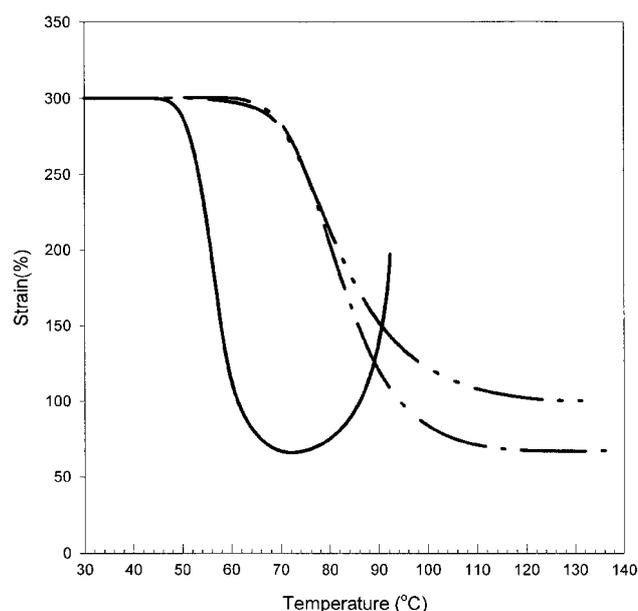


Figure 2. Percent strain versus temperature for PN (—), 50CpPN (---) and 50CyPN (-.-.-). An applied tensile stress of 0.8MPa and a heating rate of $4^\circ\text{C}/\text{min}$ are used.

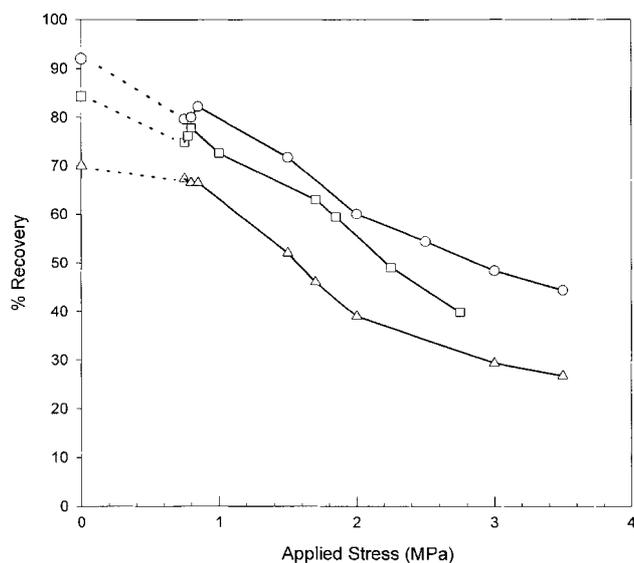


Figure 3. Percentage recovery versus various applied tensile stresses for PN (○), 50CpPN (□) and 50CyPN (△).

CpPOSS-rich domains, though neglecting a potential difference in degree of segregation/aggregation, we expect that more norbornyl segments are confined in CyPOSS domains, which increases the glass transition temperature and decreases the percentage recovery. As seen in Figs 2 and 3, 50CpPN shows enhanced percentage recovery and a higher retraction rate than 50CyPN, features we attribute to the restricted mobility of PN molecules in 50CyPN due to the relatively large CyPOSS–norbornene interaction volume.

CONCLUSIONS

In this study we have investigated the shape-memory properties of PN, 50CyPN and 50CpPN. Our preliminary data show that POSS hybrid polymers have fairly high strain recovery and, more importantly, POSS-reinforcement of PN leads to significant enhancement of the thermal stability. Therefore, POSS hybrid polymers have a great advantage for higher temperature applications. TEM of undrawn 50CyPN

and 50CpPN reveals that the POSS macromers aggregate to form cylindrical domains, the size of which is much larger for 50CyPN than for 50CpPN, with this domain size influencing thermal and shape-memory properties. Moreover, we have found a microstructural explanation for significant alteration of the shape-memory characteristics in the polynorbornene–POSS polymer systems. The driving force for shape recovery in PN is strong relaxation of such highly oriented chains which occurs during heating above the glass transition temperature. However, in the case of POSS hybrid copolymers, the PN chain segments are relatively less oriented during tensile drawing, and this is compounded by a resistance to strain recovery of the PN chain segments due to POSS–POSS interactions. The net result is enhanced retraction stability at the expense of slightly lower percentage recovery for POSS–PN copolymers. The large strain recovery values obtained, even for the large contents of the POSS comonomer employed, are afforded by the nanometer-scale distribution of POSS within the material, which enables the materials to maintain a continuous PN matrix.

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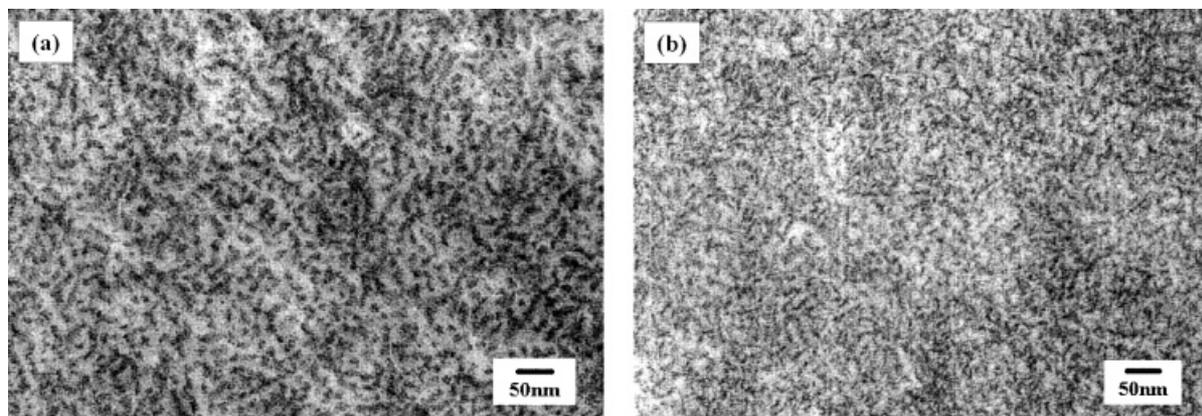


Figure 4. Transmission electron micrographs of (a) 50CyPN and (b) 50CpPN showing the different size of cylindrical structure depending on the corner groups present in POSS macromers.

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