Morphological and Mechanical Evaluation of Hybrid Organic−Inorganic Thermoset Copolymers of Dicyclopentadiene and Mono- or Tris(norbornenyl)-Substituted Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT: A new class of organic−inorganic hybrid thermoset copolymers has been prepared by ring-opening metathesis polymerization catalyzed with bis(tricyclohexylphosphine)benzylideneruthenium(II) dichloride (**1**). Dicyclopentadiene (DCPD) and norbornenylethyl polyhedral oligomeric silsesquioxane (1NB-POSS) and tris(norbornenylethyl)-POSS (3NB-POSS) with isobutyl pendent groups have been copolymerized at 60 °C over a range of POSS loadings. These copolymers contain small aggregates of 1NB-POSS, three to four molecules, at high loadings and uniform dispersions over all loadings of 3NB-POSS. The pendent group of 1NB-POSS decreases the cross-link density of the PDCPD matrix while 3NB-POSS increases the cross-link density. POSS incorporation has little effect on the glass transition temperature (T_g). Addition of 20 wt % 1NB-POSS decreases the T_g from 128 °C for PDCPD to 114 °C. Addition of 3NB-POSS has little effect on the T_g over the range of POSS loadings. The stiffness, in tension and compression, is observed to decrease with increasing POSS loading. Although the yield stress for both systems decreases, the toughness also decreases. The decrease in toughness of the 1NB-POSS copolymers is attributed to a loss of irreversible damage with increased POSS loading. Although a similar decrease in toughness is observed for the 3NB-POSS copolymers, the change in toughness is attributed to a decrease in cohesive strength with 3NB-POSS loading.

Introduction

Poly(dicyclopentadiene) (PDCPD) is a commercially important thermoset polymer as a consequence of its high modulus, impact strength, and chemical resistance.[1] PDCPD is attractive not only for its physical and mechanical properties but also for its ease of fabrication. Polymerization of DCPD with metathesis catalysts is performed using reaction injection molding (RIM) to manufacture snowmobile and boat housings, chlorine cell covers, and wastewater treatment equipment.[2] The ring-opening metathesis polymerization (ROMP) of DCPD forms a cross-linked article in a matter of minutes, at which point it can be removed from the mold and postcured.[3] DCPD is also often used as the matrix material in fiber reinforced[4,5] and rubber toughened composites.[6] Additionally, additives are incorporated to increase heat resistance[7] and the glass transition temperature (T_g).[8] To manufacture fiber reinforced PDCPD composites, fiber mats, such as glass, carbon, or aramid fibers, are impregnated, under pressure, with a mixture of DCPD and ROMP catalysts and heated to activate the catalysts.[5] For example, rubber toughened PDCPD synthesized with 2−5 wt % styrene−butadiene block copolymer generally increased the notched Izod impact resistance from 50 to 400−700 J/m.[6] At faster polymerization rates, articles with smaller rubber particles were formed, increasing the materials toughness, as expected from theory. It was concluded that with higher polymerization rates, relative to phase separation, agglomeration of the rubber particles is prevented. Additionally, additives, such as trifluoromethanesulfonic anhydride[7] and peroxides,[8] have been used to increase the cross-link density, thus increasing the heat resistance and T_g of the polymer.

Hybrid organic−inorganic composite materials are currently being studied for their physical properties that span the gap between polymers and ceramics.[9] A well-studied class of materials are exfoliated clay nanocomposites, where the included clay has one major dimension on the size scale of 1−100 nm.[10−14] Polyhedral oligomeric silsesquioxane (POSS) have also received much attention for their ability to be copolymerized with common monomers to form organic−inorganic materials.[15] These hybrid materials have the advantage of being covalently bonded to the polymer backbone, and in some cases, the morphology of the POSS aggregates can be controlled by the processing conditions.[16,17]

POSS is a monodisperse well-defined nanoparticle containing a Si_8O_{12} core with an organic periphery. New synthetic procedures allow for the synthesis of a molecule in which, in general, seven of the silicon atoms have an inert organic functionality, such as isobutyl or cyclopentyl groups, and the eighth silicon atom has a reactive group, such as a styrenyl or norbornenyl groups.[18−20] Many linear copolymers, such as polyethylene, polypropylene, polybutadiene, polystyrene, and polynorbornene, with POSS as a comonomer have been reported.[15] These polymers often exhibit increased oxidative stability, mechanical reinforcement, and morphological modification.

Epoxy-POSS thermoset systems have also been studied.[21] Multifunctional POSS, containing four epoxide groups on the periphery, copolymerized with aliphatic diepoxides and an amine-curing agent increased and broadened the T_g, increased the tensile modulus, but

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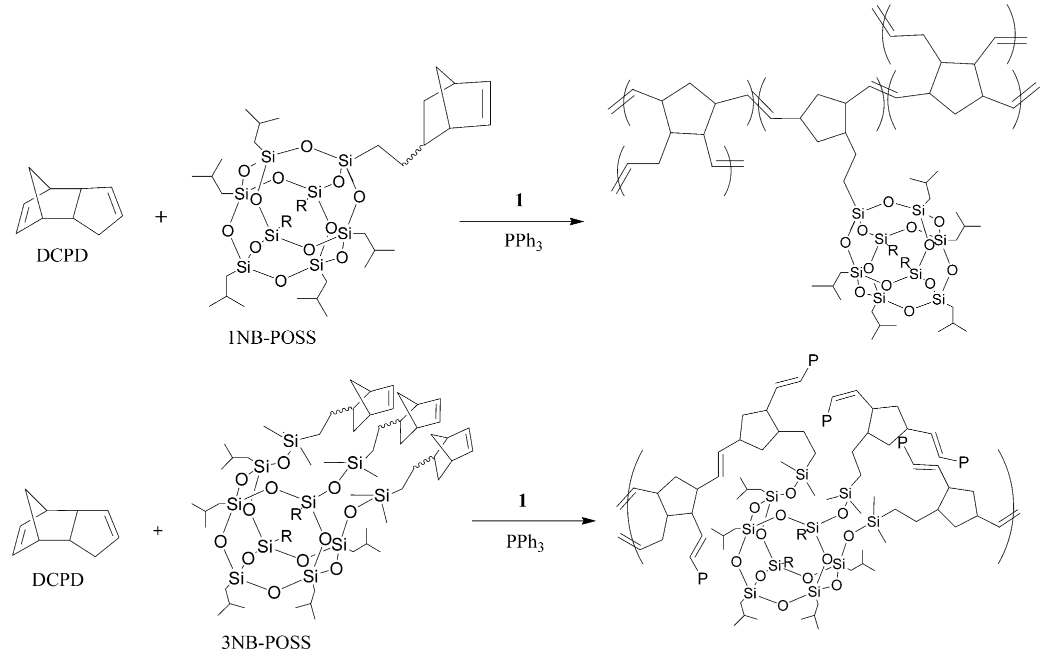
Scheme 1. Reaction Scheme for the Copolymerization of DCPD with POSS, Where R Is the POSS Isobutyl Group and P Is the PDCPD Network



lowered the flexural modulus over that of the neat epoxy resin. Incorporation of monofunctional epoxy POSS into an amine cured epoxy network increased and broadened the T_g without changing the cross-link density and enhanced the thermal properties. Additionally, it was found that the thermal and thermal−mechanical properties of a multifunctional styryl-POSS vinylester resin nanocomposites were dependent on the percentage of POSS incorporated into the resin.[22] Over a range of POSS incorporations, the T_g of the copolymers changed very little, but the flexural modulus increased with increasing POSS content.

Some initial work has been done on PDCPD−POSS copolymers.[23] By incorporating 0.1 wt % octanorbornenyl-POSS (the solubility limited amount) in PDCPD, the T_g and the storage modulus above T_g were increased over that of homopolymer PDCPD. When monofunctional POSS with a cyclopentyl periphery was incorporated into the network, the T_g decreased over that of the homopolymer. These changes were attributed to changes in the cross-link density, such that the octanorbornenyl-POSS increased the cross-link density over PDCPD homopolymer, while the monofunctional POSS lowered the cross-link density.

While there are many studies on the affects of POSS incorporation in thermoset resins, each specific POSS can behave differently in a specific resin. The changes can be attributed to factors such as the size of the POSS $(Si-O_{1.5})_n$ cage, the nature of the organic periphery, the number of reactive functionalities, and the concentration and solubility of POSS in the resin. These factors determine whether POSS is incorporated as isolated and uniformly dispersed molecules, unreacted and phase-separated particles, or matrix-bound aggregates. The different morophologies that result affect the physical and mechanical properties of the final material. In the current work, the effects of copolymerization of the mono- and tris(norbornenyl) functional, isobutyl Si_8O_{12} POSS with DCPD are reported. Specifically, the morphological, thermal, and mechanical properties of PDCPD thermoset copolymers are studied. Norbornenylethylisobutyl-POSS (1NB-POSS) and tris(norbornenylethylisobutyl)-POSS (3NB-POSS) are copolymerized with DCPD using bis(tricyclohexylphospine)benzylideneruthenium(II) chloride (**1**), forming a thermoset article (Scheme 1). The effect of POSS incorporation on the thermal and mechanical properties of PDCPD is reported. Most surprisingly, incorporation of either POSS decreases the yield stress while reducing the toughness of the material.

Experimental Section

Materials and Synthesis of PDCPD Copolymers. Catalyst **1** was purchased from Strem Chemical, 1NB-POSS was provided by the Air Force Research Laboratory, Propulsion Directorate, AFRL/PRSM, Edwards Air Force Base, CA, and 3NB-POSS was purchased from Hybrid Plastics. All other reagents were purchased from Aldrich and used as received unless otherwise noted. Dicyclopentadiene was melted and purified by passing through warm activated basic alumina. Stock solutions of **1** and triphenylphosphine (PPh_3) in dry and degassed benzene were prepared and kept frozen until needed. Solutions of DCPD and 10 or 20 wt % added POSS were copolymerized. DCPD, POSS, PPh_3, and **1** were measured as molar ratios of 15 000 equiv of norbornenyl unsaturations to 2 mol equiv of PPh_3 to 1 mol equiv of **1**. For example, the reaction mixture for PDCPD-*co*-1NB-POSS with 20 wt % added POSS was composed of 34.5 g (0.261 mol) of DCPD, 6.91 g (7.37 mmol) of 1NB-POSS, 14.8 mg (0.018 mmol) of **1** in approximately 20 μL of benzene, and 9.4 mg (0.036 mmol) of PPh_3 in approximately 30 μL of benzene. The addition of PPh_3 was necessary to reduce the activity of the catalysts to allow sufficient time to fill the molds before gelation. Plaques were made by mixing the reactants in a beaker and pouring into a mold made from sandwiching a 3 mm thick PTFE spacer between 2 sheets of $^1/_2$ in. thick plate glass. The glass plates were treated with a PTFE mold release prior to filling. The mold was placed into an oven at the cure temperature (60 °C) for 24 h and postcured at 100 °C for 4 h unless otherwise stated. Compression samples were made in a similar fashion in which the DCPD/POSS was poured into 18 mm diameter test tubes and cured as stated. It is important to note that the 1NB- and 3NB-POSS copolymers were synthesized from different lots of DCPD, and slight changes in the physical properties of the homopolymers were observed. Therefore, each

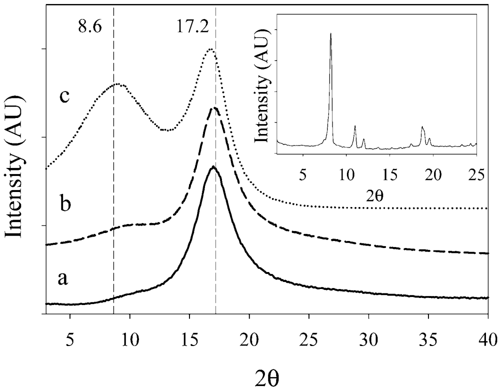


Figure 1. Wide-angle X-ray diffraction spectra of 1NB-POSS copolymers: (a) PDCPD homopolymer, (b) 10 wt % added POSS, (c) 20 wt % added POSS. The ordinate is offset for clarity. Inset shows the spectra of 1NB-POSS monomer.

POSS copolymer system will be compared to PDCPD homopolymer cured from the same lot.

Characterization. Wide-angle X-ray diffraction (WAXD) was performed using a D500 X-ray diffractometer with Cu Kα irradiation (wavelength of 1.54 Å) using a nickel filter. The X-rays were collimated with a pinhole collimator. Data points were collected over a range of 2°−40° 2θ at 0.05 intervals with 10 counts per interval. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA 2980. Samples were analyzed in tension at 1.0 Hz over a temperature range of −100−200 °C at a ramp rate of 3 °C/min. Typical samples were 5 mm long, 3 mm wide, and 1 mm thick. The amplitude of oscillation was set at about 6 mm, imposing a strain of 0.1%. The T_g was determined as the peak of the alpha transition in the loss modulus. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2050 thermogravimetric analyzer at a heating rate of 20 °C/min from room temperature to 700 °C with a continuous purge of nitrogen (100 mL/min) or air (60 mL/min).

Mechanical measurements were performed in tension and compression on an Instron 1123 machine. Samples were prepared according to ASTM D638 for tensile and ASTM D695 for compression tests. Tensile samples were loaded at a constant crosshead speed of 5 mm/min, and compression samples were loaded at crosshead speeds of 0.5, 5, and 50 mm/min at 25, 50, and 75 °C. Compact tension specimens, for fracture toughness tests, were cut according to ASTM D5045 and precracked with a razor blade. Specimens were load at a constant crosshead speed of 100 mm/min. Optical micrographs of the damage zone around the fractured surface of the compact tension specimens were taken at 5× magnification under cross-polarizers with an Olympus BX60 optical microscope with an attached Sony CCD IRIS/RGB color video camera.

Results and Discussion

Network Morphology. The morphology and aggregation of POSS were analyzed by wide-angle X-ray diffraction (WAXD). Waddon et al. have found that single crystals of POSS monomer form hexagonal arrays in which the organic units change the ratio of the lattice parameters but maintain the crystalline geometry.[24] For linear copolymers, it has been shown that the processing conditions and the amount of POSS incorporated into the polymer chains can control the extent of aggregation.[16] In the current system, aggregation is dictated by the solubility of POSS in the DCPD matrix and the rate of the cross-linking reaction, which freezes the morphology at gelation. In the solid state, 1NB-POSS monomer forms aggregates that can be observed in the WAXD spectra (Figure 1, inset). 1NB-POSS has a sharp peak at 8.2° 2θ, corresponding to a d spacing of 10.8 Å. (A detailed analysis of the crystal structure of 1NB-POSS can found in ref 24.) It has been reported, for linear copolymers, such as polyethylene-*co*-POSS, that as POSS loading in the copolymer increases, larger aggregates of POSS form.[17] This is also true for the 1NB-POSS PDCPD copolymers cured at 60 °C. The spectrum of PDCPD shows a diffuse amorphous halo at 17.1° 2θ with a d spacing of 5.18 Å and a length calculated by Scherrer's equation of 58.2 Å (Figure 1). This peak has been attributed to scattering of C and H atoms in the backbone, similar to that of scattering observed in polynorbornene.[25] Only at 20 wt % added 1NB-POSS does POSS aggregation occur, in which a broad peak at 8.6° 2θ is observed. Analysis of the peak reveals a d spacing of 10.3 Å and a length of 35.2 Å as calculated by Scherrer's equation. Presumably, these aggregate are composed of approximately three to four POSS molecules. This illustrates that POSS stays well dispersed in the medium rendering optically clear amber materials (due to the presence of residual catalyst). In the interest of assembling larger 1NB-POSS aggregates, PDCPD-*co*-1NB-POSS (20 wt % added POSS) was cured at lower temperatures (40 and 50 °C) to determine whether slower reaction rates would allow for increased POSS aggregation. Similarly sized aggregates of three to four 1NB-POSS molecules were observed when cured at 40 °C. In comparison, aggregation is not observed in the 3NB-POSS copolymers cured at 60 °C. 3NB-POSS is a viscous liquid in which crystallization is hindered by the three norbornenyl groups; only amorphous scattering is observed for the monomer and copolymers. Therefore, the isobutyl periphery is highly soluble in the DCPD matrix, allowing for well-dispersed 1NB and 3NB copolymers. Some insight can be found in a report for an amine cured epoxy based on bisphenol A, in which the glycidylisobutyl-POSS is soluble in the diamine and insoluble in the epoxy resin.[26] Addition of the epoxy to the amine/POSS mixture causes separation into a POSS-rich phase and an epoxy-rich phase with small POSS aggregates. Separation is purely due to immiscibility of the isobutyl-POSS with bisphenol A. This suggests that changing the organic periphery of the POSS to something less soluble in the PDCPD matrix, possibly a phenyl group, should promote aggregation.

Copolymer densities were measured according to ASTM D792 in 23 °C water, purified by reverse osmosis. Density increases linearly with POSS loading for both systems (Table 1). The densities of the monomers have been estimated to be 1.13 g/cm^3 for 1NB-POSS and 1.601 g/cm^3 for 3NB-POSS. Calculations utilizing these values and the density of the respective PDCPD homopolymer reveal that the densification is in agreement with the rule of mixtures.

Thermal Properties. Cross-link density was analyzed by equilibrium swelling in *p*-xylene at 75 °C in accordance with literature procedures.[8] For 1NB-POSS the cross-link density decreases linearly with POSS loading (Figure 2). This behavior is expected since 1NB-POSS acts as a chain extender, and more importantly, the POSS cube fills volume in which cross-linking can no longer occur. This is approximately 14 nm^3 per POSS molecules, assuming a hard sphere with a diameter of 1.5 nm. In comparison, 3NB-POSS behaves as a cross-linking site because of the increased functionality. The presence of the three norbornenyl groups increases the cross-link density linearly with POSS loading. This trend is also reflected in the T_g of the copolymers.

Table 1. Properties of 1NB-POSS and 3NB-POSS Copolymers

copolymer	ρ^a (g/cm^3)	ρ^b (g/cm^3)	T_g (°C)	E^c (GPa)	$\sigma_y{}^c$ (MPa)	E^d (GPa)	$\sigma_y{}^d$ (MPa)	V^{*f} (nm^3)	ΔH^f (kJ/mol)	$E_a{}^f$ (kJ/nm^3)
0% 1NB	1.047 ± 0.003	1.047	129	0.930 ± 0.020	60.5 ± 0.5	1.54 ± 0.01	66.4 ± 1.0	3.17	265.0	83.6
10% 1NB	1.055 ± 0.002	1.055	128	0.870 ± 0.020	55.1 ± 0.2	1.37 ± 0.03	52.8 ± 0.1	4.82	325.0	67.4
20% 1NB	1.062 ± 0.003	1.063	114	0.808 ± 0.300	44.7 ± 0.3	1.42± 0.05	47.8 ± 0.7	4.74	330.8	69.8
0% 3NB	1.042 ± 0.002	1.042	137	0.892 ± 0.064	52.6 ± 0.3	1.36 ± 0.05	71.2 ± 0.2	3.17	248.7	78.4
10% 3NB	1.044 ± 0.002	1.044	144	0.836 ± 0.031	46.0 ± 0.3	1.27 ± 0.02	65.0 ± 0.3	4.31	289.3	67.1
20% 3NB	1.046 ± 0.001	1.046	137	0.758 ± 0.009	42.5 ± 0.1	1.24 ± 0.02	60.6 ± 0.2	4.24	269.1	63.4

[a] Average density of three samples as measured by ASTM D792. [b] Density predicted by the rule of mixtures. [c] Average tensile modulus (E) and tensile yield stress (σ_y). [d] Average compressive modulus (E) and compressive yield stress (σ_y). [f] Quantities are calculated from compression data using Eyring's model of solid flow; V^* = activation volume of yielding, ΔH = enthalpy of yielding, E_a = activation energy density of yielding.

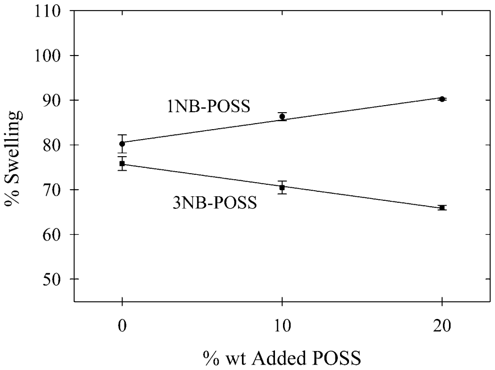


Figure 2. Equilibrium swelling in *p*-xylene at 75 °C of 1NB and 3NB-POSS copolymers for evaluation of cross-link density.

Addition of 1NB-POSS decreases the T_g from 128 to 114 °C when 20 wt % is added. In terms of cross-link density, it would be expected that the T_g of the 3NB-POSS systems would increase with POSS loading. But little change is observed in the T_g of the 3NB-POSS copolymers with respect to PDCPD homopolymer. A recent report characterizing the effect of POSS content on the T_g of poly(acetoxystyrene-*co*-styrylisobutyl-POSS) copolymers give insight into the T_g shifts in the current system.[27] It was found that at low POSS loadings, less than 3−4 mol %, POSS acts as an inert diluent, interrupting dipole−dipole interactions. At higher POSS contents, POSS−POSS interactions dominate as aggregates form, increasing the T_g. Molecular dynamics simulations of poly(norbornene-*co*-POSS) (PN-POSS) by Farmer revealed that chain packing around the organic periphery had a large influence on T_g.[25] Cyclopentyl-POSS copolymers show a greater enhancement in T_g than cyclohexyl-POSS copolymers due to more efficient packing around the cyclopentyl groups. In the current system, the organic periphery is composed of flexible isobutyl groups and the maximum POSS loading is 2.7 mol % added 1NB-POSS, within the diluent regime. Furthermore, both 1NB- and 3NB-POSS stay well dispersed, virtually eliminating POSS−POSS interactions, allowing the diluent effect to dominate over cross-link density. For 10 wt % added 1NB-POSS or 3NB-POSS the POSS concentration is not substantial enough to cause a pronounced decrease in T_g. At 20 wt % of either POSS moiety, the diluent effect is more pronounced and dominates the excess cross-linking of the 3NB-POSS system.

The diluent nature of the POSS moiety is also apparent from the lower temperature transitions observed in the PDCPD copolymers. While no new transitions are observed with the incorporation of POSS, the dynamic mechanical spectra shows shifts and amplification of the alpha prime ($T_{\alpha'}$) and beta (T_β) transitions (Figure 3). For the 1NB-POSS copolymers, $T_{\alpha'}$ can be observed as a peak, or shoulder, near the T_g peak in the loss modulus trace. The $T_{\alpha'}$ for PDCPD homopolymer is well-defined and separated. As POSS loading increases, this peak becomes less defined and the peak temperature slightly increases with addition of 10 wt % but decreases at 20 wt % added POSS. For the 3NB-POSS copolymers, this transition occurs at a lower temperature due to the change in DCPD monomer. As 3NB-POSS loading increases, the intensity of the $T_{\alpha'}$ transition increases and the peak shifts to higher temperatures. Additionally, the beta transition in both POSS systems intensifies and shifts to lower temperatures (−5 to −24 °C) with POSS loading. Mather was able to relate the occurrence of a low-temperature transition in PN-POSS copolymer (−50 °C for cyclopentyl POSS) to the organic periphery of the POSS.[28] Although the beta transition is already apparent in the PDCPD homopolymer, the shift and amplification are likely influenced by the isobutyl periphery.

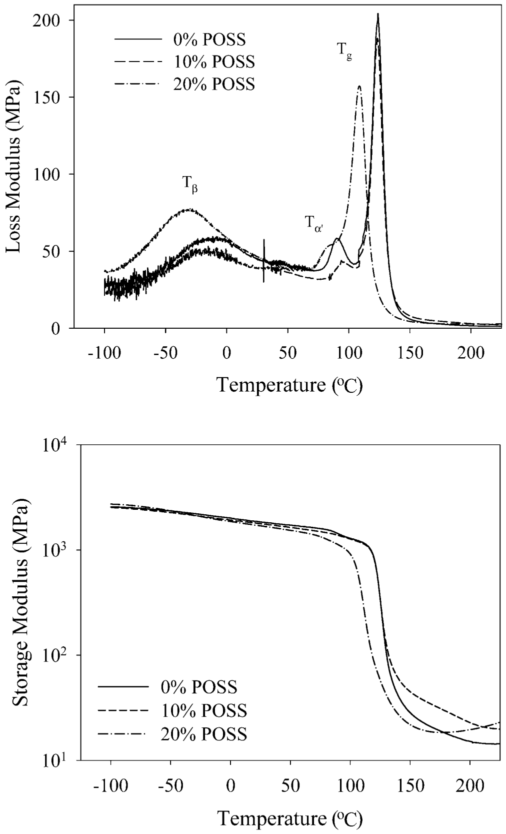


Figure 3. Loss and storage modulus of 1NB-POSS copolymers. Data were attained with an oscillation frequency of 1 Hz and a heating rate of 3 °C/min.

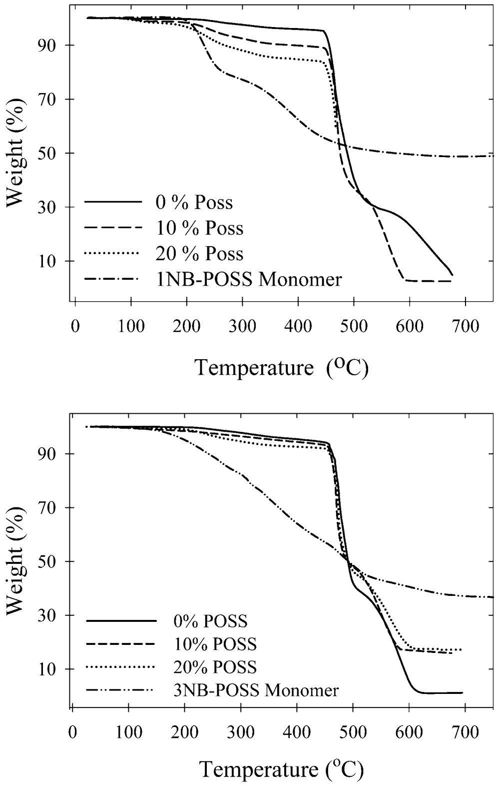


Figure 4. TGA traces of 1NB-POSS copolymers (top) and 3NB-POSS copolymers (bottom) in air with a flow rate of 60 mL/min and a heating rate of 20 °C/min.

Thermogravimetric analysis of the copolymers was performed in both nitrogen and air. Under nitrogen PDPCP homopolymer undergoes 15% weight loss at 300 °C followed by decomposition at 495 °C with little char yield. Copolymers of 1NB- and 3NB-POSS showed similar results with up to 20% weight loss at 300 °C and decomposition at 495 °C with little char yield. Above 300 °C, and in N_2, POSS sublimes, accounting for the increase in copolymer decomposition. More importantly, it has been shown that POSS enhances the thermal oxidative stability of many copolymers.[29] Thermogravimetric analysis in air reveals that PDCPD homopolymer loses only 6–10 wt % before decomposing at 455 °C with little char yield (Figure 4). The increased stability of PDCPD before decomposition is due to oxidative cross-linking through unsaturations in the backbone.[30] Once again, the addition of POSS does not change the main decomposition temperature but increases the level of decomposition before 455 °C. From calculations, 55% of the mass of 1NB-POSS monomer and 64% of 3NB-POSS is aliphatic and the remainder inorganic. The thermogram of 1NB-POSS monomer reveals that most of the aliphatic material is lost by 300 °C, which corresponds to the plateau in the thermogram. The increased decomposition of the copolymers before 455 °C corresponds to decomposition of 1NB-POSS. Figure 5 shows that there is good correlation between the aliphatic weight of the added POSS to the copolymer weight lost by 455 °C. In comparison, 3NB-POSS has higher thermal oxidative stability than 1NB-POSS. Thermogravimetric traces of the monomer reveal that the aliphatic material is not totally lost until 500 °C, and the residual inorganic material does not decompose. There is only a small increase in decomposition of the 3NB-POSS copolymers before 455 °C. Therefore, the additional decomposition of the copolymers can be accounted for by the decomposition of POSS.

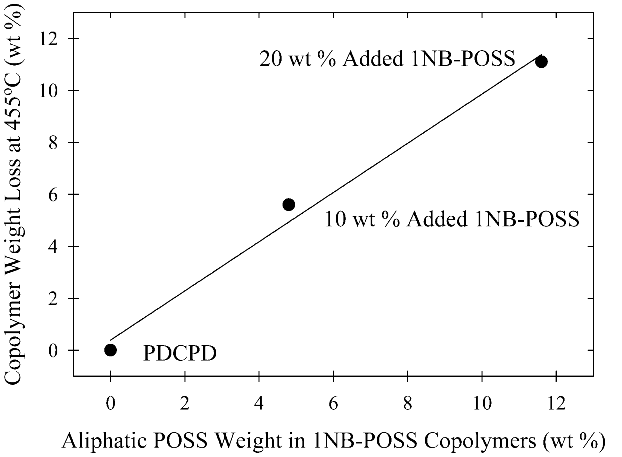


Figure 5. Relationship between the extent of decomposition of the 1NB-POSS copolymers before 455 °C to the weight of 1NB-POSS in each copolymer at 455 °C. The slope of the trend line is 0.94.

Mechanical Evaluation. Addition of POSS, 1NB-POSS, or 3NB-POSS decreases the modulus and yield stress in tension and compression (Table 1). In tension, these materials yield at approximately 9% strain, neck, draw, and finally fail at approximately 25% strain for 1NB-POSS and 14% strain for 3NB-POSS. The modulus decreases with POSS loading for either system. The yield stress is also observed to decrease with POSS loading for both POSS systems. In terms of cross-link density, the results for 1NB-POSS would be expected since cross-link density is proportional to yield stress. For 3NB-POSS it was expected that the yield stress would increase due to the increase in cross-link density. This was not observed; the yield stress decreases with POSS loading, but the change is not as significant as with the 1NB-POSS copolymers. Similar results were found in compression, with the exception that the modulus is decreased by 10% for both POSS systems and plateaus by 20 wt % added POSS. To further investigate the yielding behavior, the thermodynamic properties for yielding were calculated. The effects of strain rate and temperature on yield can be utilized in Eyring's model for solid flow to analyze the effect of POSS on the activation volume (V^*), enthalpy (ΔH), and activation energy density (E_a) for yielding (eq 1).

$$\frac{\sigma_y}{T} = \frac{2}{V^*}\left[\frac{\Delta H}{T} + 2.303R\log\left(\frac{\epsilon_y{}^*}{\epsilon_0{}^*}\right)\right] \qquad (1)$$

For both systems the expected temperature and rate dependence were observed, and the yield stress decreases with POSS loading (Figure 6). The calculated activation volumes and enthalpies increase and plateau with the addition of either POSS (Table 1). This leads to a lower activation energy density for yielding. Therefore, although 3NB-POSS has a higher cross-link density, the copolymer has lower activation energy density, and thus the material yields more easily regardless of the number of the reactant group.

Since the yield stress of these materials decreases with POSS loading, an increase in fracture toughness would be expected. However, measurement of the fracture toughness, K_{1C}, reveals that the toughness of each system decreases with POSS loading, irrespective

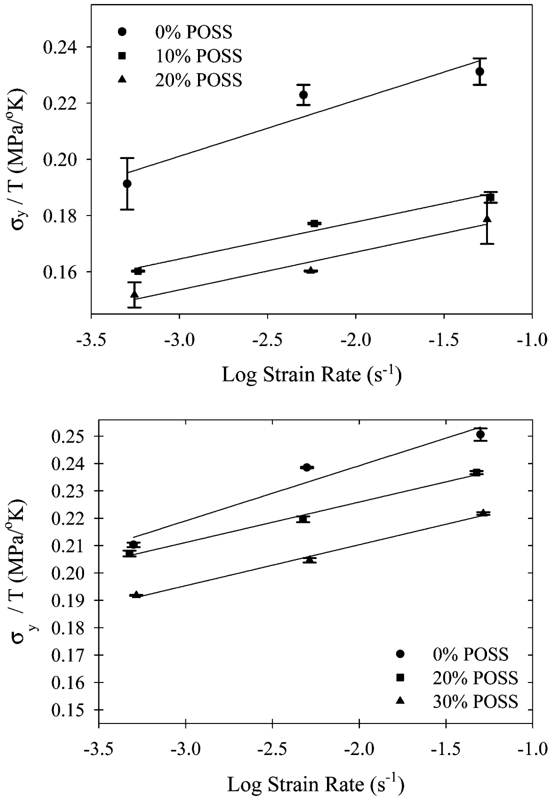


Figure 6. Rate dependence of the yield behavior, in compression, on 1NB-POSS copolymers (top) and 3NB-POSS copolymers (bottom). Each point is the average of three samples.

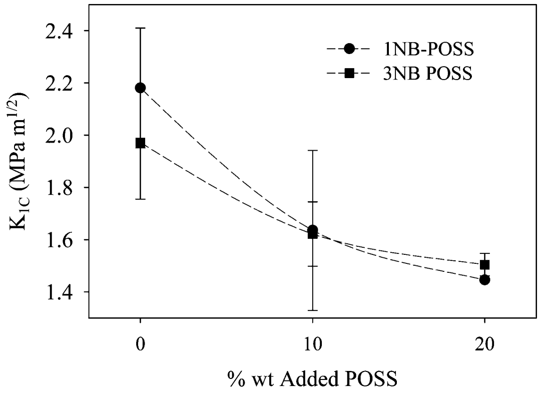


Figure 7. Change in fracture toughness of 1NB- and 3NB-POSS copolymers with POSS loading. Trend lines are placed through the data for clarity.

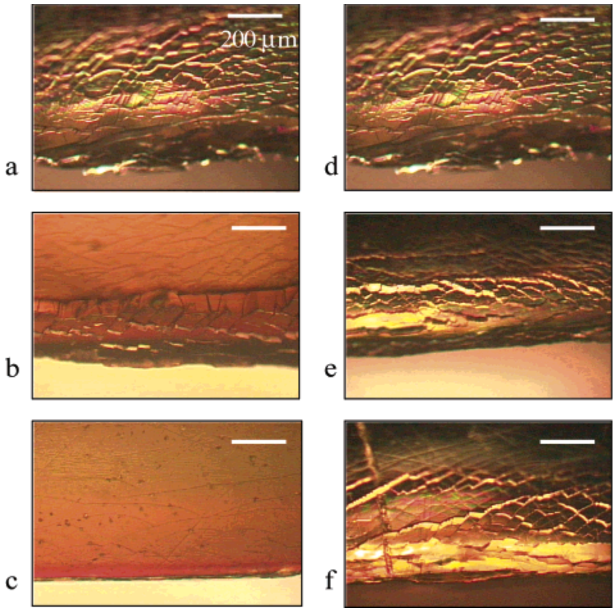


Figure 8. Optical microscope images of the compact tension specimens' process zone under cross polarizers at 5× magnification. Images a−c are of 1NB-POSS copolymers: (a) 0, (b) 10, and (c) 20 wt % added POSS. Images d−f are of 3NB-POSS copolymers: (d) 0, (e) 10, and (f) 20 wt % added POSS. Scale bars are 200 μm in length.

of the type of POSS (Figure 7). To further evaluate this behavior, optical micrographs of the fracture surface and process zone were analyzed. Micrographs of PDCPD homopolymer show that yielding and irreversible damage have occurred (Figure 8a,d). For the 1NB-POSS copolymers, the size of the process zone and the irreversible damage decrease with POSS loading (Figure 8b,c). At 20 wt % added 1NB-POSS there is no apparent sign of yielding. Since fracture toughness is enhanced by yielding and irreversible damage, these observations are in agreement with the measured decrease in toughness. Similar analysis of the 3NB-POSS copolymers reveals that yielding and irreversible damage occur at all loadings (Figure 8e,f). Although the 3NB-POSS copolymers show a similar decrease in toughness as the 1NB-POSS copolymers, a similar trend in yielding and damage is not observed. The lower fracture toughness, in conjunction with the decrease in yield stress, suggests that a decrease in the cohesive strength of the polymer occurs with commensurate increase in POSS loading.

Conclusion

PDCPD-*co*-POSS copolymers are a unique class of organic−inorganic thermoset copolymers. The synthetic methodology allows for synthesis of covalently bonded and well-dispersed inorganic moieties. At high 1NB-POSS loadings aggregates of approximately three to four POSS molecules are found, while 3NB-POSS remains uniformly dispersed over all loadings. The thermal and mechanical reinforcement that is characteristic of linear copolymers with POSS is not observed in this system. POSS loading slightly decreases the thermal oxidative resistance of the copolymer before the primary decomposition temperature of the PDCPD network due to the lower thermal stability of POSS. The modulus and yield stress, in tension and compression, of the copolymers decrease with POSS loading, irrespective of the cross-link density. An unexpected characteristic of the system is that the fracture toughness also decreases with POSS loading. For 1NB-POSS, the decrease in toughness is in agreement with the loss of irreversible damage occurring during fracture. For the 3NB-POSS copolymers, yielding and irreversible damage are observed at all loadings. The decrease in toughness may be due to a decrease in cohesive strength with POSS loading. The results suggest that the nature of the organic periphery and the overall size of the POSS moiety have a greater influence on the properties of the copolymers than the cross-linking nature of the reactive group.

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Supporting Information Available: Addition morphological, thermal, and mechanical characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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