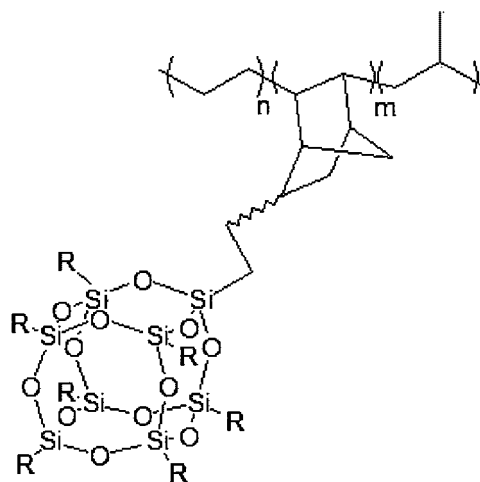


Ethylene–Propylene–Silsesquioxane Thermoplastic Elastomers

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Preparative methods for the incorporation of polyhedral oligomeric silsesquioxane (POSS) macromonomers into ethylene–propylene (EP) polymers have been developed that utilize metallocene polymerization. Analysis of these novel ethylene–propylene–POSS polymers using wide-angle X-ray diffraction reveals that pendant POSS groups off the polymer backbones aggregate with a phenyl periphery, and the polymers crystallize as anisotropically shaped nanocrystals. POSS particle aggregation is strongly dependent on the nature of the POSS peripheral group. X-Ray studies suggest that aggregation of POSS in the EP elastomers did not occur with isobutyl and ethyl peripheries, as they disperse within the polymer matrix. The formation of POSS nanocrystals increases the mechanical properties of these thermoplastic elastomers. The tensile storage modulus increases significantly with the addition of POSS, as does the length of the rubbery plateau region. Tensile studies reveal an elongation at break of 720% for one EP-phenyl POSS polymer sample, with the others between 400 and 500%.



Introduction

Polymeric nanocomposites have become an important area of research.^[1–4] Polymer nanocomposites are polymers that have been reinforced, either by blending or chemical incorporation, with nanostructured materials. Conventional composites, which have domain sizes on the micrometer level, have properties that are dependent upon the properties of each component weighted by the volume

fraction. Another important parameter in composites is interfacial interactions between component phases, which cause material properties to be higher than predicted in conventional composites, and will play a more important role as the domain sizes decrease. When the domain sizes are at the nanometer level, material properties are more strongly influenced by interfacial interactions than bulk material properties.^[1] This gives rise to the importance of nanocomposites. Nanocomposites have a potential use in many fields, such as automotive, sporting goods, optics, electronics, templates, and many others.^[1–4]

One class of materials that can be used to prepare nanocomposites is polyhedral oligomeric silsesquioxanes (POSS). POSS is a general name to describe organic–inorganic materials with cubic caged structures that contain silicon and oxygen atoms, with a silicon-to-oxygen ratio of 1 to 1.5.^[1,5] The POSS core is surrounded

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by peripheral groups off each silicon atom, which can consist of aliphatic, aromatic, or aryl groups, as well as other functional groups. POSS is synthesized by the controlled hydrolysis of trialkoxy- or trichlorosilanes. This synthesis produces a variety of products, which include ladder and straight chain silsesquioxanes, as well as completely condensed and partially condensed cage structures of varying sizes. Completely condensed caged structures are used as polymer fillers or crosslinkers if the POSS peripheral contains multiple reactive functional groups. A partially condensed cage structure allows for the addition of a single reactive functionality, which can subsequently be used for copolymerization or grafting reactions. POSS nanocomposites are an example of an organic–inorganic hybrid material. These hybrid materials are advantageous, as they combine the strong thermal and oxidative properties of inorganic materials with strength and processibility of organic materials.^[1,5,6]

There have been significant research efforts on POSS-containing copolymers, including polystyrene,^[7,8] poly(methyl methacrylate),^[9,10] polyethylene,^[11–14] polyimide,^[15] polynorbornene,^[16] and styrene–butadiene–styrene (SBS) triblock copolymers,^[17–19] to name but a few examples. In general, POSS incorporation into polymers increases the glass transition temperature, oxidative resistance, surface hardening, and tensile strength of the hybrid polymers. An important property of POSS is the ability to aggregate in copolymers, thus creating physical interactions between polymer chains. This aggregation can be thought of as a physical crosslink, which could be utilized in elastomers.

Elastomers are amorphous materials that undergo long, reversible deformations.^[20] Typical properties of pre-crosslinked elastomers are low glass transition temperatures and low secondary forces. These polymers are then chemically crosslinked, most frequently by sulfur or peroxides. Crosslinking gives elastomers their strong mechanical and elastic properties. There are many classes of elastomers, including diene, saturated hydrocarbon, halogenated, nitrile, inorganic, and thermoplastic. Thermoplastic elastomers are the only class that does not require chemical crosslinks, as they gain their strength from physical interactions between polymer components. For example, in triblock copolymers of SBS, styrene domains phase separate to form these stable physical crosslinks. The styrene domains can be disrupted with either heat or dissolution, and reformed by cooling the polymers or by evaporating off the solvent.^[20–22]

Despite the intensive research on POSS copolymers with semi-crystalline and amorphous polymers, there has been little work on POSS molecules chemically incorporated in sub-ambient glass transition temperature (T_g), amorphous polymers. These materials are interesting as thermoplastic elastomers, where POSS can act as a physical crosslink. One

example of thermoplastic elastomers that contain POSS is poly(butadiene-co-POSS), synthesized by the ring-opening metathesis polymerization of 1,5-cyclooctadiene and cyclopentylPOSSnorbornene.^[23] In these random copolymers, POSS was observed to aggregate into two-dimensional (2D) aggregates at low POSS loadings, with POSS domain lengths as long as 50 nm. At higher POSS loadings, the POSS formed large, 2D raft-like structures with a length scale of micrometers. Although POSS was shown to aggregate in these polymers, their mechanical properties could not be studied because of the poor thermal and mechanical properties of the relatively low-molecular-weight butadiene-based copolymers. Therefore, it is of interest to study POSS aggregation in elastomeric materials with stronger material properties, such as ethylene–propylene–diene monomer (EPDM) elastomers, which contain three components: ethylene is used to give the material mechanical strength, propylene disrupts the crystallinity of the polymer, and a diene is used in subsequent crosslinking reactions.^[20] Because of their strong mechanical, thermal, and weatherability properties, EPDM elastomers find applications ranging from seals for automobiles, to hoses, tubing, footwear, and roofing materials.^[20,24] In the current study, POSS was chemically incorporated into ethylene–propylene copolymers. In these novel thermoplastic elastomers, the aggregation of POSS was studied while changing the POSS peripheral group. Mechanical studies were performed to study the effectiveness of POSS physical crosslinks in thermoplastic elastomers.

Experimental Part

Materials

Toluene, hexanes, tetrahydrofuran (THF), and triethylamine were purchased from Aldrich and purified by vacuum distillation from calcium hydride. Isobutyl-POSS-norbornene macromonomer, 1-[2-(5-norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-hepta-isobutylpentacyclo[9.5.1.1^{3,9}.1^{5,11}.1^{7,13}]octasiloxane, ethyl-POSS-norbornene, 1-[2-(5-norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,11}.1^{7,13}]octasiloxane, and trisilanol-phenyl-POSS, 1,3,5,7,9,11,14-hepta-phenyltricyclo[7.3.3.1^{5,11}]heptasiloxane-endo-3,7,14-triol, were purchased from Hybrid Plastics, and used as received. Norbornylethyl trichlorosilane was purchased from Oakwood Products and used as received. The polymerization catalyst, ethyl(bis-indenyl)hafnium dichloride was purchased from Boulder Scientific. Methaluminoxane (MAO), 10%, was purchased from Albemarle.

Synthesis of Phenyl-POSS-Norbornene

In an example reaction, at room temperature, 1.07 mmol (1 g) of trisilanol-phenyl-POSS was stirred in 30 mL of THF in a 100 mL round bottom flask with a septum under a nitrogen atmosphere. Next, 1.09 mmol (0.280 g) of norbornylethyl trichlorosilane was

added. Finally, 3.35 mmol (0.339 g) of triethylamine was added dropwise; clouding of the reaction solution was immediately observed. The reaction was stirred overnight. In the work-up, the solvent was removed under vacuum, and the resulting solid was redissolved in diethyl ether. The solution was filtered to remove the triethylamine-HCl salt, and precipitated into excess acetonitrile. Isolated yields were greater than 75%. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.6\text{--}7.3$ (aromatic, 5H), 6.04 (olefin, 1H), 5.97 (endo), 5.82 (olefin, 1H), 2.74 (1H), 2.68 (1H), 2.50 (endo), 2.01 (1H), 1.81(1H), 1.31 (1H), 1.28 (2H), 1.10 (endo) 0.85 (2H), 0.46 (2H).

^{13}C NMR: $\delta = 133.1, 131.2, 129.7, 129.4, 126.8, 48.4, 43.8, 41.4, 40.8$ (endo), 40.3, 31.2, 26.4, 9.6.

^{29}Si NMR: $\delta = -78, -65$.

Polymerization of Ethylene-Propylene-POSS Terpolymers

Reactions were performed in an Autoclave Engineers Zipperclave 0.5 L stainless steel reactor, with controlled heating, gas flow, and mechanical stirring.^[25,26] Prior to polymerization, the reactor was heated to 70 °C, purged with nitrogen gas for 90 min, and cooled to room temperature. In an inert atmosphere drybox, a solution of POSS in toluene was prepared; also added was 1 mL of MAO to scavenge any impurities. Separately, a solution of 15 mg of ethyl(bis-indenyl)hafnium dichloride and MAO, with a 1 000: 1 MAO-to-catalyst ratio, was prepared and aged for 30 min before injection into the reactor, in order to obtain maximum catalytic activity. The POSS solution was added to the reactor and stirred with ethylene and propylene gas. The reactor was stirred at 1 250 rpm and heated to 40 °C. Each reagent gas was allowed to flow into the reactor by separate mass flow controllers. The total pressure was set at 50 psi with an apparent 50: 50 gas ratio. Next, the catalyst solution was added to the reaction mixture. Ethylene and propylene gas were continually allowed to flow into the reactor to maintain a reactor pressure of 50 psi. Gas flow was monitored through the Julabo, a customized LabView automated computer program. The reactions were stopped by releasing the pressure in the vessel and precipitating the polymer in a solution of 10% HCl/methanol. Residual POSS monomer was removed by consecutive precipitations of a toluene/polymer solution into ethyl acetate. The terpolymers were filtered and dried in a vacuum oven at 50 °C overnight.

Polymer Characterization

^1H NMR spectra were obtained in CDCl_3 or CD_2Cl_2 on a Bruker DPX-300 FT-NMR spectrometer operating at 300 MHz. ^{13}C NMR spectra were obtained at 90 °C in tetrachloroethane- d_2 on a Bruker 400 FT-NMR spectrometer operating at 100 MHz. ^{29}Si NMR spectra were obtained in tetrachloroethane- d_2 on a Bruker 400 FT-NMR spectrometer operating at 80 MHz. Gel permeation chromatography data was obtained using a Polymer Laboratories PL-GPC 50 Integrated GPC System, using THF as the mobile phase. Molecular weights were calibrated against narrow molecular weight polystyrene standards.

Differential Scanning Calorimetry (DSC)

DSC was performed under a nitrogen atmosphere on a DuPont Instruments DSC 2910. Samples were cooled to $-110\text{ }^\circ\text{C}$ and heated at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Data was obtained on second heating.

Thermal Gravimetric Analysis (TGA)

TGA was performed using a Mettler–Toledo TGA/SDTA851^o. Samples were heated at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to 800 °C in an air atmosphere.

Wide Angle X-Ray Diffraction (WAXD)

WAXD patterns were obtained on a PANalytical X'Pert PRO instrument in reflectance mode. Samples for this study were prepared by dissolving the polymer in a toluene solution, and casting it onto a glass slide. The solvent was allowed to evaporate over 2 h. Residual solvent was driven off by heating the sample at 40 °C for 24 h in a vacuum oven.

Dynamic Mechanical Analysis (DMA)

DMA was performed on a TA Instruments AR 2980 Dynamic Mechanical Analyzer, in tensile mode, using a frequency of 1 Hz. The samples were prepared in a manner similar to that for WAXD studies.

Tensile Tests

Samples for tensile tests were prepared by casting a film from a 10% solution in toluene. Samples were dried at 45 °C overnight. Dog bone shaped specimens were cut from the film, with testing lengths of 22 mm and widths of 4 mm. Samples were pulled at a rate of $20\text{ mm}\cdot\text{min}^{-1}$. Each sample was tested 4 to 5 times, and an average of the curves was calculated. In the cyclic tests, films were pulled to 100% elongation at $20\text{ mm}\cdot\text{min}^{-1}$ and relaxed back to a zero displacement at the same rate. This was repeated four times. Next, the sample was pulled to 200% elongation and allowed to relax back to zero displacement. This was repeated four times. The same procedure was used at 300% elongation. This 15-step cyclic test was performed on each sample twice. Experiments were performed on an Instron 5500R.

Results and Discussion

Polymerization

Ethylene–propylene–POSS (EPPOSS) terpolymers were synthesized using the hafnium-based metallocene catalyst, ethyl(bis-indenyl)hafnium dichloride (Scheme 1). Traditionally, EPDMs have been synthesized using vanadium-based Ziegler–Natta catalysts.^[20] These catalysts effectively synthesize EPDMs, but suffer from multi-modal distributions, poor diene incorporation, and difficulty in removal of alkylaluminum chloride cocatalysts. More recently, however, there have been many research efforts on the synthesis of EPDMs using metallocene-based

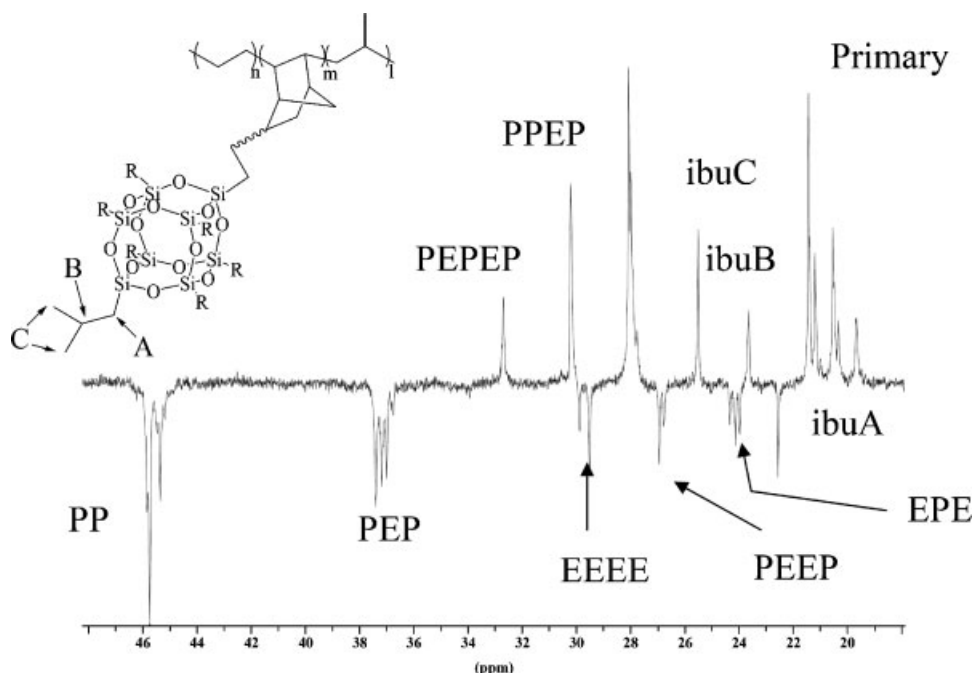


Figure 1. DEPT135 NMR of EPIbuPOSS copolymers. Peak assignments based upon the literature^[33] show ethylene(E) and propylene(P) sequences.

catalysts, which give unimodal polymer distributions with sufficiently high molecular weights, good propylene and diene incorporation, relatively low polydispersities, and easier removal of cocatalysts.^[27–32] In one example, a series of metallocene catalysts were used to synthesize EPDMs, using MAO cocatalysts.^[32] One catalyst, ethyl(bis-indenyl)hafnium dichloride, was able to synthesize EPDM elastomers with high molecular weights

($\bar{M}_w > 500\,000 \text{ g} \cdot \text{mol}^{-1}$), relatively low polydispersities ($\approx 2\text{--}2.5$), and good comonomer incorporations. The results for the ethylene propylene POSS terpolymerizations are shown in Table 1.

Polymerizations took place under an apparent 50:50 ethylene-to-propylene ratio. According to literature precedence, the same reaction conditions produced ethylene-propylene copolymers with 59 mol-% ethylene

Table 1. Summary of molecular weight data of EP-POSS polymers.

Reaction ID	POSS in polymer ^{a)}	POSS in polymer	E: P ^{a)}	\bar{M}_n ^{b)}	PDI ^{b)}
	mol-%	wt.-%	mol	$\text{g} \cdot \text{mol}^{-1}$	
EP	0	0	35: 65	70 000	2.09
Ibu5	0.3	5	25: 75	73 000	1.77
Ibu16	0.7	16	52: 48	76 000	1.73
Ibu22	1.3	22	32: 68	65 000	2.03
Ibu30	1.6	30	34: 66	57 000	1.57
Ph10	0.4	10	50: 50	113 000	2.07
Ph21	0.9	21	48: 52	86 000	2.07
Ph30	1.4	30	50: 50	75 000	1.70
Ph36	1.7	36	59: 41	37 000	2.80
Et20	1.0	20	52: 48	41 000	1.41
Et30	2.0	30	50: 50	19 500	4.70

^{a)}As determined from ^{13}C or ^1H NMR in CD_2Cl_2 or $\text{C}_2\text{D}_2\text{Cl}_4$; ^{b)}As determined by GPC in THF vs. narrow molecular weight polystyrene standards.

incorporation.^[32] The POSS periphery was altered to include isobutyl (Ibu), ethyl (Et), and phenyl (Ph) peripheries. However, the reactions using IbuPOSS had low ethylene incorporations, which indicates a deviation from the expected ratio. POSS incorporations ranged from 5 to 36 wt.-%, with sufficiently high molecular weights and moderate polydispersities. All samples had unimodal molecular weight distributions, except for Ph36 and Et30. The Ph36 sample had two overlapping peaks, nearly identical in size. In the Et30 sample, two nearly equal peaks with a combined molecular weight of $19\,500\text{ g}\cdot\text{mol}^{-1}$ and a polydispersity of 4.7 were observed. Polymers that contained PhPOSS generally had higher molecular weights and higher than expected ethylene-to-propylene ratios. EtPOSS terpolymers had lower molecular weights than either IbuPOSS or PhPOSS terpolymers.

The ethylene and propylene peak assignments were taken from the literature.^[33] The presence of ethylene runs, propylene runs, alternating sequences, and random sequences indicates a random ethylene–propylene microstructure, as shown in Figure 1. POSS incorporation was determined from the integration of the methyl peaks of the isobutyl periphery (Ibu C), and compared to the integrations of the ethylene–propylene sequence peaks. This method was also used to determine EtPOSS incorporation. In PhPOSS polymers, the POSS incorporation was determined directly by ^1H NMR spectroscopy, as the chemical shift of the aromatic POSS proton resonances were compared to the olefinic ethylene–propylene resonances, which have chemical shifts further upfield. These values were compared to the ethylene–propylene ratio from ^{13}C NMR spectra to determine monomer incorporations.

WAXD Studies

WAXD was used to study the aggregation of POSS in the ethylene–propylene matrix. Figure 2 shows the X-ray diffraction patterns of EPIbuPOSS terpolymers. The bottom trace is an ethylene–propylene (EP) copolymer. Going from the bottom trace upwards, the IbuPOSS incorporation in the terpolymers increases. The top trace is of the IbuPOSS monomer. The EP copolymer has a broad peak centered at a 2θ value of 18, which indicates an amorphous polymer. There are, however, two sharp peaks within this broad peak, indicative of backbone ethylene crystallization.^[34] These peaks are only observed in the EP and EPIbu22 samples, which indicates an amorphous EP polymer in all other samples. The IbuPOSS monomer has the most intense diffraction peak at a 2θ value of 8, which is indicative of POSS monomer crystallization, as POSS monomers crystallize into three-dimensional hexagonal arrays. However, when POSS is chemically incorporated into polymers, their packing is constrained to 2D sheets due to geometric

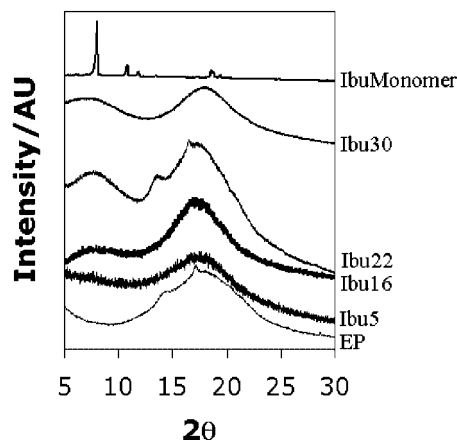


Figure 2. WAXD pattern of EPIbuPOSS polymers.

constraints of attaching a POSS pendent group to a polymer chain. This results in broadening of the X-ray diffraction peaks. In the case of these IbuPOSS polymers, WAXD patterns show broad diffraction peaks centered at a 2θ value of 8. This suggests either POSS dispersion within the EP polymer matrix or the formation of very small POSS aggregates. Although it is of interest that IbuPOSS disperses within the EP matrix, this study requires POSS aggregation to determine their applicability as physical crosslinks for thermoplastic elastomers. Therefore, the POSS periphery was altered to include chemical moieties with less favorable interactions with ethylene–propylene elastomers, namely a phenyl and ethyl periphery. WAXD patterns of the series of EPPhPOSS (left) and EPETPOSS (right) samples prepared are shown in Figure 3.

In PhPOSS polymers, as the POSS incorporation is increased, the diffraction peak at a 2θ value of 8 increases in intensity, with much sharper diffraction peaks than in the IbuPOSS polymers. This is indicative of POSS crystallization. As was observed with the IbuPOSS copolymers, EtPOSS polymers show broad diffraction peaks, which indicates that EtPOSS also disperses within the EP matrix. This is of great interest, as by simply altering the POSS periphery, POSS can be engineered to either disperse or aggregate within a specific polymer matrix. The polymer films prepared for these studies further reinforce this interpretation. The IbuPOSS and EtPOSS polymers were qualitatively softer than the EP parent polymer, which indicated that the dispersed POSS acts as a plasticizer, rather than as physical crosslinks. These two samples also lacked sufficient strength for DMA studies, unlike the PhPOSS polymers. The sample preparation method was also studied to determine if POSS aggregation could be driven by thermal annealing or slow solvent evaporation. Samples were cast from toluene solutions, allowing for either fast evaporation of solvent (2 h), or slow evaporation (7 d). They were also prepared by pressing ($150\text{ }^\circ\text{C}$ at 5 000 psi for 5 min) or annealing ($120\text{ }^\circ\text{C}$ for 7 d). The WAXD

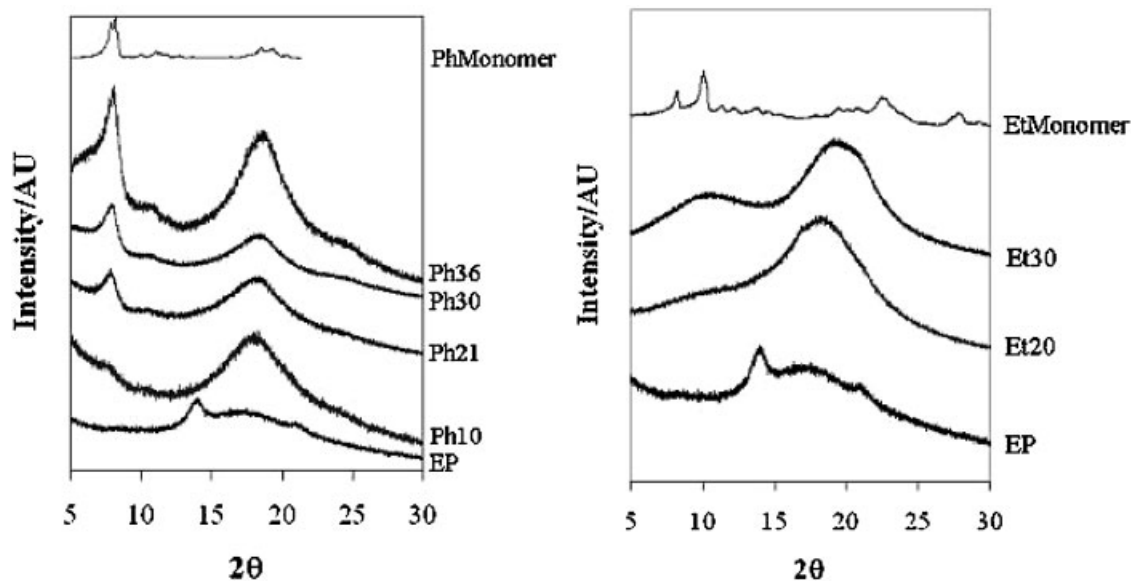


Figure 3. WAXD data of EPhPOSS (left) polymers and EPtPOSS (right) terpolymers.

results are shown in Figure 4. The EPh36 samples show sharper diffraction peaks at 2θ values of 8 by both annealing and pressing the samples, which indicate a more ordered structure in the polymer films. In both the annealed and pre-annealed EPh36 sample, there is a sharp diffraction peak preceded by a broader peak, which indicates the existence of both POSS aggregates and either smaller aggregates or dispersed POSS particles. This broad peak does not appear in the pressed sample. In the EPh21 sample, annealing the sample resulted in a sharper POSS diffraction peak, which indicates larger aggregate sizes. Although altering the preparation method had an impact on the PhPOSS polymers, it had no impact on POSS aggregation in EtPOSS and IbuPOSS polymers, as

peripheral interactions with the EP domain allow only for POSS dispersion or formation of small aggregates.

Using Scherer's equation, the sizes of the POSS domains can be estimated from WAXD data. In Scherer's equation, $L = 0.9\lambda/\beta \cos\theta$, where L is the domain length, λ is the wavelength of the X-ray, β is the peak width at half maximum, and θ is the angle. This calculation has previously been performed to estimate POSS domain sizes.^[35] In these calculations, it is assumed that POSS has a 15 Å diameter. The results from these calculations are shown in Table 2. This method simply estimates the

Table 2. Estimation of POSS domain sizes using Scherer's equation.

Sample	Domain size	≈POSS per domain
	nm	
Ph36	5.3	3–4
Ph36annealed ^{a)}	6.3	4–5
Ph36pressed ^{b)}	9.5	6–7
Ph30	7.8	5–6
Ph21	7.1	4–5
Ph21annealed ^{a)}	9.5	6–7
Et30	1.1	1
Ibu30	2.1	1–2
Ibu22	2.7	1–2
Ibu16	1.3	1

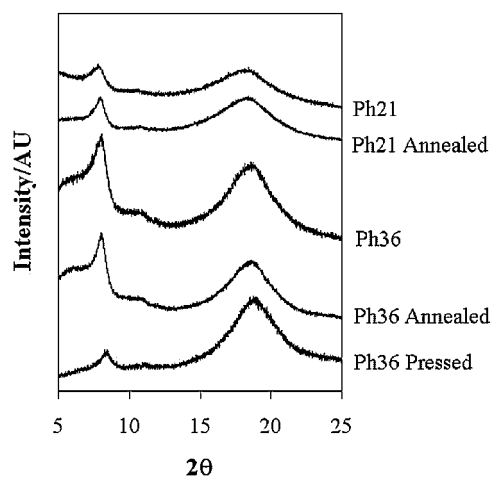


Figure 4. WAXD patterns for EPhPOSS copolymers by different preparation methods.

^{a)}Film was annealed at 120 °C in a vacuum oven for 7 d; ^{b)}Film was formed by pressing the raw sample at 150 °C and 5 000 psi for 5 min.

largest domain size, with the number of POSS molecules it takes to fill a domain this size. POSS aggregates could also form in other directions, with the other dimension having either one or two POSS cubes. Therefore, the number of POSS molecules per domains is probably larger than this estimated value. These results show that the PhPOSS copolymers have larger domain sizes than the EtPOSS and IbuPOSS copolymers, as Ph21, Ph30, and Ph36 samples have domain lengths of 7.1, 7.8, and 5.3 nm, respectively. The length of all of the ethyl or isobutyl POSS periphery polymers, however, was on the order of 1–2 POSS molecules, proving these samples lack POSS aggregation. Larger domain sizes can be driven in the PhPOSS polymers by annealing or by pressing. For example, the Ph21 domain length increases from 7.1 to 9.5 nm by annealing the sample.

Thermal Characterization

A summary of the thermal characterization of all EPOSS terpolymers is shown in Table 3. All data from DSC were obtained on second heating, where only a single glass transition temperature was observed from –110 to 200 °C for EPOSS samples. The DSC data show a surprising invariant relationship between T_g and POSS incorporation. Generally in literature reports, the incorporation of POSS into low T_g polymers causes an increase in T_g with increasing POSS loading, as the large bulky side POSS chain slows polymer mobility. The ethylene-to-propylene ratio varies in most of the different polymers, which is also

known to affect the glass transition temperature. As the propylene content in an EP copolymer increases from 50 to 70%, the T_g increases. The ethylene-to-propylene content varies greatly in the IbuPOSS copolymers. In the PhPOSS and EtPOSS copolymer, the ethylene-to-propylene ratio appears to be more constant, but there is an inherent error involved in the determination of this ratio by quantitative ^{13}C NMR spectroscopy. This could account for the invariant T_g values.

The TGA data is shown in Table 3, which was performed under an air atmosphere. Here, both the 2% decomposition temperature and char yields are reported. The literature trend shows an increase in decomposition temperature of POSS-containing copolymers versus the homopolymer.^[5] In these EPOSS polymers, mixed results are observed. In the best case, EPibu16 shows a greater than 80 °C increase in 2% decomposition temperature versus the EP homopolymer. There are also, however, several samples that show only moderate increases in decomposition temperature. The EtPOSS copolymers show the lowest decomposition temperatures. This is expected, as EtPOSS-norbornene has a 2% decomposition temperature of 193 °C. The increase in decomposition temperature could be a result of POSS aggregating at the surface of the material. POSS not only decomposes at a higher temperature than EP copolymers, but when POSS decomposes under an air atmosphere, it is able to form silica.^[5] Silica is stable at temperatures much higher than the 800 °C used in these studies. Therefore, POSS could form a silica layer at the surface, which should protect the underlying polymeric material from decomposition.

Table 3. Thermal characterization of EPOSS terpolymers.

Polymer	POSS	T_g (DSC) ^{a)}	2% Decomp. temp. ^{b)}	Char yield	Theoretical char yield ^{c)}
	wt.-%	°C	°C	%	%
EP	–	–44	243	3.5	0
Ibu5	5	–38	216	13.9	4.1
Ibu16	16	–47	329	6.2	7.2
Ibu22	22	–42	306	10.5	11.2
Ibu30	30	–42	183	24.8	15.4
Ph10	10	–51	250	9.6	3.8
Ph21	21	–52	327	10.0	8.1
Ph30	30	–49	281	19.0	11.6
Ph36	36	–48	308	19.2	13.9
Et20	20	–46	277	11.7	11.3
Et30	30	–50	250	9.6	16.9

^{a)}DSC data was obtained on second heating, heating from –100 to 200 °C, at 10 °C · min^{–1}; ^{b)}TGA data was obtained by heating to 800 °C at 20 °C · min^{–1}; ^{c)}Theoretical char yields were calculated assuming a complete conversion of POSS into SiO₂.

Another important factor in TGA studies of POSS-containing polymers is the char yield. The char yield should increase with increasing POSS loadings, as there are more POSS cages able to form silica char. The EP copolymers show a low char yield, as completely saturated hydrocarbon polymers form little or no char. An increase in char yield with increasing POSS loading is generally observed. A theoretical char yield can also be calculated, assuming a complete conversion of POSS into silica. Comparing these calculations to the actual values, there are cases in which less char is formed than expected, which indicates an incomplete conversion of POSS to silica. There are also cases where the char is greater than expected, especially with the PhPOSS polymers. Aromatic rings are also known to form char, which could account for the higher than expected char yields.

DMA Studies

Films of EPPhPOSS polymers were prepared for DMA studies. The results of these studies are shown in Figure 5. The PhPOSS polymers show promising results. The storage modulus in the glassy region has an invariant relationship with POSS loading, as Ph21 has the highest modulus, followed by Ph10, Ph36, Ph30, and EP. This could be a result of the various copolymer configurations at sub- T_g temperatures. Although the EPPh36 data was obtained on second heating, the trend still fits with all samples on first heating. All other samples show the same mechanical results in the glass transition region, the rubber plateau region, and the rubbery flow region on first and second heating. The glass transition temperatures are more in line with expectations based on literature precedence, as the T_g increases with

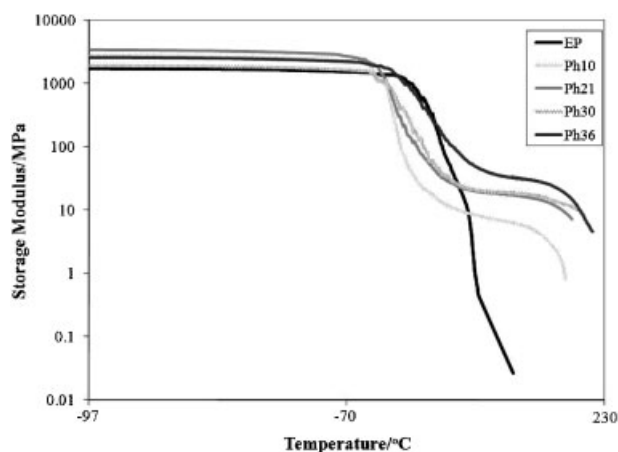


Figure 5. DMA of EPPhPOSS polymer samples from -97 to 230 °C. Plot shows the storage modulus as a function of temperature. Samples were heated from -100 to 200 °C at 5 K per minute. Arrow shows increasing POSS content in terpolymers.

increasing POSS loading. The EP copolymer has a higher value, which is because of the different ethylene-to-propylene ratio than the EPPhPOSS copolymers.

The rubbery plateau region is important to determine if POSS is acting as a physical crosslink. Crosslinked materials show an extension of the rubbery plateau region and an increase in the modulus of the rubbery plateau region as compared to the non-crosslinked polymer counterpart.^[32] The storage modulus in the rubbery plateau region increases with increasing POSS loading, with Ph36 having the highest modulus, Ph30 and Ph21 being nearly equal, and Ph10 being the lowest. At room temperature, Ph36 shows a significant increase in storage modulus over the EP copolymer, with values of 37.1 MPa and 0.3 MPa respectively. These values relate to the size of POSS aggregate domains, as determined from WAXD studies. The Ph30 sample has the largest domain size of 7.8 nm, followed by Ph21 with 7.1 nm and Ph36 at 5.3 nm. Although Ph30 has a higher POSS incorporation than Ph21, it has larger domain sizes, thus fewer crosslink junctions. The Ph21 sample has more crosslink junctions, which results in similar modulus values as Ph30. Although Ph36 has a slightly higher POSS incorporation, it has much higher storage modulus values because it has smaller domain sizes, thus more crosslinking junctions than Ph21 or Ph30. This data demonstrates the strong increase in tensile properties with the addition of POSS to copolymers.

The transition of the samples from the rubbery plateau region to the rubbery flow region correlate to the dispersion of the POSS aggregates. The Ph10 sample has the lowest value of 93 °C (Table 4). The other samples have values between 135 and 140 °C, which shows that higher temperatures are required to disperse polymers with a higher number of crosslink junctions and/or larger POSS domain sizes. The length of the rubbery plateau region increases greatly with the POSS incorporation, as compared to the EP parent polymer. Therefore, the addition of POSS aggregates creates a larger rubbery plateau region.

Table 4. DMA data.

Sample	T_g	T_g	Rubbery plateau region	G' at 25 °C
	(DSC)	(DMA) ^{a)}		
	°C	°C	°C	MPa
EP	-44	-24		0.3
Ph10	-51	-46	-28 to 93	7.2
Ph21	-52	-45	-14 to 135	18.3
Ph30	-49	-40	-15 to 135	19.2
Ph36	-48	-31	-1 to 140	37.1

^{a)}Determined from the maximum of $\tan \delta$.

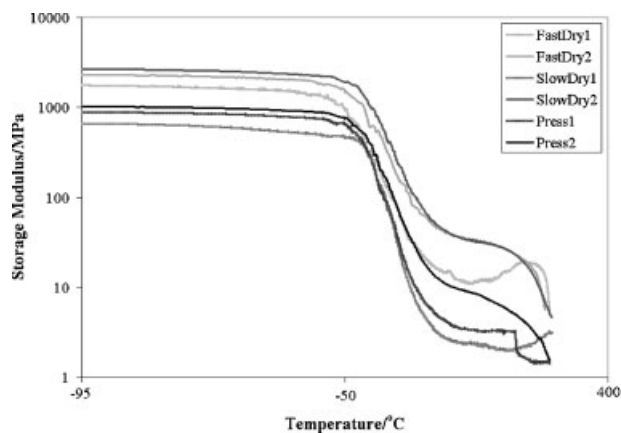


Figure 6. Dynamic mechanical study of EPPh36 polymers, with varying polymer film preparation techniques, including a slow evaporation method (7 d), fast evaporation (2 h), and by pressing the sample at 5 000 psi at 150 °C. Each sample was heated from –100 to 200 °C twice, at a rate of 5 K per minute, using a frequency of 1 Hz and with an initial force of 0.05 N. This plot measures the storage modulus as a function of temperature.

This result indicates that POSS acts as a physical crosslink for thermoplastic elastomers, assuming POSS aggregation in the copolymers.

The method of preparation of the EPPh36 polymer films provides materials with different mechanical properties. DMA data for EPPh36 were obtained on samples prepared by fast and slow solvent evaporation methods, as well as melt pressing. The results are shown in Figure 6. Each sample was cooled to –100 °C, heated to 200 °C, cooled back down to –100 °C, and heated back to 200 °C. All samples were completely soluble after the second heating, which indicates that no chemical crosslinking had occurred. The fast and the slow evaporation methods show similar results. In the case of the fast evaporation method during the first heating, the storage modulus is relatively low. When the sample is heated above 110 °C, there is an increase in the storage modulus. This is indicative of a change in the microstructure of the polymer. According to WAXD studies, the Ph36 sample contains larger POSS aggregates, as well as small aggregates or dispersed POSS particles.

The increase in the modulus of this material could be a result of the formation of POSS aggregates from these small aggregates or dispersed POSS molecules. Above 160 °C, the storage modulus drops off, which indicates a dispersion of POSS aggregates. The sample prepared by the slow evaporation method shows similar results, as the storage modulus of the sample increases over 110 °C, and up to 200 °C. Upon second heating, the results change drastically. The storage modulus in the glassy region increases with both evaporating technique samples, showing similar values. This remains true

across the other regions of the graphs, as much stronger tensile properties are obtained with the more ordered POSS polymers. This occurs despite the fact that the molecular weight of the samples are decreasing with increased POSS loading. Therefore, POSS has a large impact on material properties.

This study shows that different evaporation methods produce samples that need to be heated and strained to produce microstructures conducive to stronger mechanical properties. The samples prepared by the pressing method produce different results. The first heating shows relatively low mechanical properties. Upon second heating, the pressed sample has a slightly higher storage modulus, which remains lower than the other samples on their second heating. The pressed sample might have a higher density, thus lower mobility, making it more difficult for the ordering of POSS domains. This is supported by the T_g of the materials. The T_g of the pressed sample is 8 °C higher than the other samples, indicating less free volume, thus a more dense material.

Tensile Tests

Tensile tests were performed on each of the EPPhPOSS samples. Dog bones were cut from toluene cast films. The results are shown in Figure 7. The stress–strain relationship of EPOSS polymers are typical of elastomers.^[20] The EP parent polymer curve lies between Ph30 and Ph21. Although it would normally be expected that the EP sample would lie below Ph10, this result is not surprising, as WAXD studies show the EP parent polymer is semi-crystalline. Therefore, the elastic modulus of the polymer will be higher than that of an amorphous copolymer due to polyethylene crystallites. Other than the EP sample, the EPPhPOSS curves show an expected

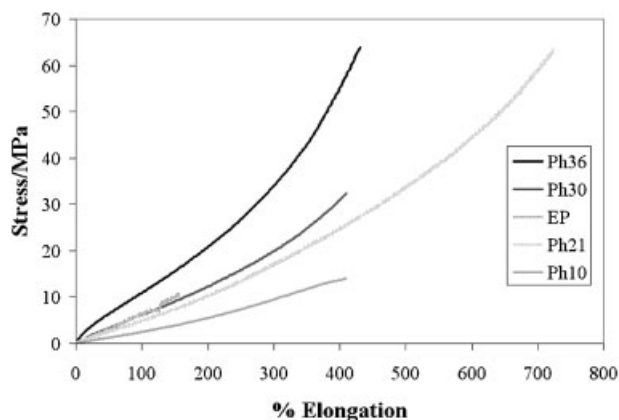


Figure 7. Tensile tests on EP and EPPhPOSS polymers, pulled at a rate of 20 mm · min⁻¹. Each sample was tested four times, and the graph values represent an average of the combined tests.

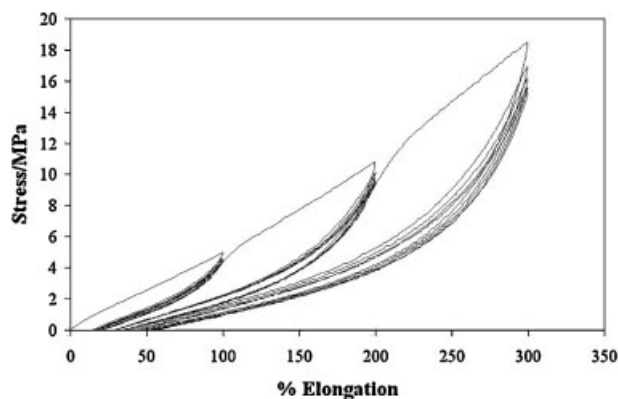


Figure 8. Cyclic tensile tests on an EPPh21 dog bone sample. During the test, a sample was stretched to 100% elongation and allowed to relax back to zero displacement five consecutive times at a rate of $20 \text{ mm} \cdot \text{min}^{-1}$. Next, the sample was stretched to 200% elongation, upon which the same five cycles were run. This was followed by five cycles at 300% elongation.

trend of an increase in elastic modulus with an increasing POSS incorporation, as increasing the number of POSS cages will increase the number of physical crosslinks, thus increasing the elastic modulus. The percent elongation at break of elastomers is typically in the range of 500–700%. Most of the EPPhPOSS elastomers lie just below this range, at 450–470%, as shown in Table 5. The EPPh21 sample, however, has an elongation at break of 720%. This polymer may have an ideal combination of POSS loading and crosslink sites, as compared to the other EPPhPOSS elastomers. The Ph30 and Ph36 samples have the highest volume fractions of the glassy POSS phase, which accounts for a decrease in their elastic properties. These strong properties help support the indication that POSS aggregates behave as physical crosslinks for thermoplastic elastomers.

Cyclic tensile tests were also performed on each of the EPPhPOSS samples, to determine possible hysteresis in the polymer samples. A typical result is shown in Figure 8.

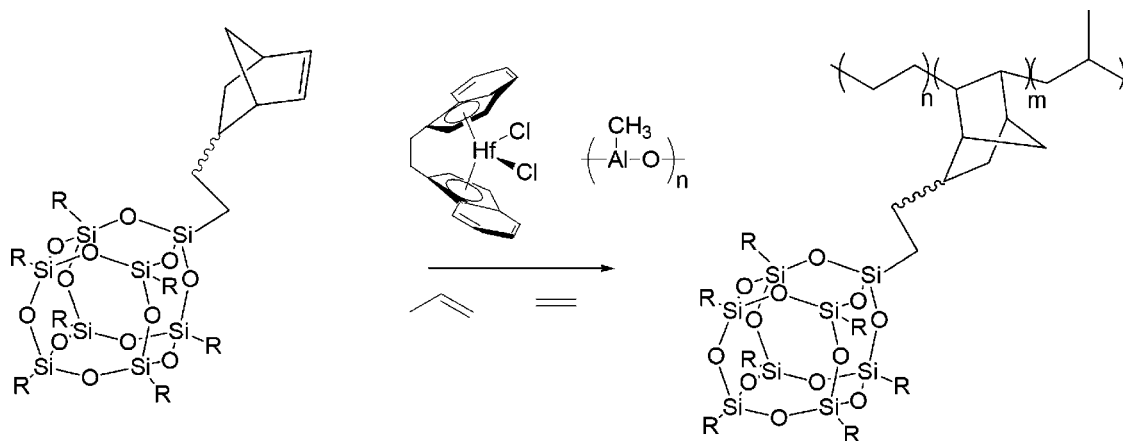
Table 5. Tensile properties of EP and EPPhPOSS samples from tensile tests.

Sample	Elongation at break	Elastic modulus
	%	MPa
EP	170	10.2
Ph10	472	5.1
Ph21	723	10.2
Ph30	448	13.4
Ph36	450	19.3

The EPPhPOSS samples show intriguing results. After the first cycle at each elongation, the sample does not return to its initial length, as the elastomers display hysteresis. However, the concurrent four cycles show very little hysteresis, and are similar to each other. This is a clear example of the Mullins effect, which occurs in positively reinforced filled elastomers.^[36,37] This effect is observed at each elongation, and also occurs in the other EPPhPOSS samples. This effect could be caused by the formation of an equilibrium physical structure after the first elongation. Upon concurrent elongations, a new equilibrium value is reached. This equilibrium value changes once again when the sample is elongated to higher values.

The main differences between the material response of the different EPPhPOSS samples are the relative deformations. Also, the EPPh10 sample breaks during the 12th cycle. The EPPh10 sample has a final deformation of 38%, whereas Ph21 has a final deformation value of 37%, Ph30 is 75%, and Ph36 is 88%. As the POSS incorporation in the polymer is increased, there is a higher volume fraction of a glassy phase. Because of this, the material is less elastic at higher loadings, as indicated by these final deformations.

Overall, the EPPhPOSS polymers show strong mechanical properties. The increase in the length of the rubbery plateau region and the increase in modulus in the rubbery



Scheme 1. Synthesis of EPPhPOSS elastomers.

plateau region, as compared to the EP copolymers indicate POSS is acting as a physical crosslink. These materials are advantageous over crosslinked EPDM elastomers, as they are able to be reprocessed, while retaining strong mechanical properties.

Conclusion

The synthesis of novel ethylene–propylene–POSS terpolymers allows for the study of POSS aggregation in a mechanically robust and amorphous ethylene–propylene polymer matrix. Polymerizations using a hafnium-based metallocene catalyst afforded random terpolymers with sufficiently high molecular weights, relatively low polydispersities, varying POSS incorporations and peripheries, and varying ethylene to propylene ratios. Thermal studies of the terpolymers show an invariant relationship between POSS incorporation and glass transition temperature, due to the varying E/P ratios. Thermal gravimetric analysis studies show an increase in decomposition temperature by incorporating POSS, but an invariant relationship between the quantity of POSS incorporation and decomposition temperature. Aggregation studies by WAXD suggest POSS disperses within the ethylene–propylene matrix with the isobutyl and ethyl peripheries, but aggregates with the phenyl periphery. This hypothesis is reinforced by mechanical tests. Terpolymers with the isobutyl and ethyl peripheries were not sufficiently strong for this mechanical test, suggesting POSS acts as a plasticizer when dispersed within the polymer matrix. EPPHPOSS elastomers show strong mechanical properties: the storage modulus of the terpolymers increases with increasing POSS loading in the rubbery plateau region, as compared to the ethylene–propylene parent polymer. The length of the rubbery plateau region also increases drastically, as compared to the ethylene–propylene parent polymer, which indicates that POSS acts as an effective physical crosslink for use in thermoplastic elastomers. Tensile studies of EPPHPOSS polymers show an increase in the elastic modulus with increasing POSS loading, as well as elongations at break as high as 720%. Cyclic tests on the EPPHPOSS elastomers show hysteresis on initial deformations. However, concurrent cycles show indications of the Mullins effect. These mechanical tests show that POSS acts as a physical crosslink, which can be utilized in thermoplastic elastomers.

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