Nanostructured Polyurethane/POSS Hybrid Aqueous Dispersions Prepared by Homogeneous Solution Polymerization

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ABSTRACT: Aqueous polyurethane dispersions were prepared with 4−10 wt % of functionalized polyhedral oligomeric silsesquioxanes (POSS) via homogeneous solution polymerization in acetone followed by solvent exchange with water. The use of acetone as the initial polymerization solvent allowed for the facile incorporation of both diamino and dihydroxy functional POSS monomers in a homogeneous reaction environment. After addition of water and removal of the acetone, stable dispersions with unimodal particle sizes were obtained. The incorporation of the POSS monomers did not have a significant effect on the dispersion's properties; however, the physical properties of the isolated polymers did display significant changes, with notable increases in storage modulus, T_g, complex viscosity, and surface hydrophobicity. These changes were attributed to the incorporation of the POSS residues into the polyurethane hard segment domains found. Though no sign of any gross phase heterogeneity due to the inclusion of POSS moieties was detected by either thermal characterization or wide-angle X-ray diffraction (WAXD), a significant change was observed by atomic force microscopy (AFM) when the samples were recast from organic solvent.

Introduction

The incorporation of polyhedral oligomeric silsesquioxanes (POSS) into based polymer composites has emerged as unique route to prepare high-performance materials for various applications. The POSS component can be incorporated through either simple melt/solution blending or can be chemically incorporated through the use of functionalized POSS monomers. With molecular dimensions on the order of a single nanometer, the POSS component has the ability to fully integrate on a truly molecular basis with the polymer matrix. Significant property enhancements have been reported for some of the POSS−polymer hybrid systems, including increased toughness, decreased flammability, ultraviolet stability, and oxidation resistance. In most cases the enhanced properties are achieved at levels of POSS incorporation (<10%) that are far below the levels needed for traditional fillers.[1−14]

Recently, there have been a number of investigations into polyurethane/POSS hybrids. These have focused on the reaction of functional POSS monomers into polyurethanes via melt processing or as solutions in organic solvent. As with other polymer systems, many of the POSS hybrids do yield elastomeric polyurethane with improvements in physical and thermal properties at relatively low levels of POSS incorporation.[15−18]

Widespread use of such materials as adhesive or coatings applications would be limited by the needs and conditions under which these products are used. Solid thermoplastic polyurethanes are limited to use as hot melt adhesives, and the organic solvent based polyurethanes are increasingly restricted in their traditional applications by environmental legislation.[19,20] These regulations along with abatement costs and safety are shifting the base technologies toward aqueous polyurethane dispersions prepared with low levels of organic solvent to gain in market usage.

An exception is the work reported by Turi and Levi on the preparation of polyurethane/POSS hybrid aqueous dispersions.[21] In their work ionomeric polyurethanes for dispersions were made by inclusion of a dihydroxy functional POSS monomer into the prepolymer reaction. Analysis of dried films subsequently prepared from these samples showed no enhancement of the polymer's physical properties or changes to the polymers thermal behavior. Assessment of the morphology showed the presence of crystalline POSS domains separate from both the polyurethanes soft and hard segment domains. Though not stated by the authors, examination of the synthesis scheme and intermediate analysis leaves open the possibility that the POSS monomers were not fully reacted in the prepolymerization step.

The dispersions reported on by Turi and Levi were prepared via a prepolymer mixing process. This process calls for the dispersing into water of an isocyanate functional prepolymer prepared from diisocyanates and polymeric diols (in this case also a POSS diol) with 15 wt % *N*-methylpyrrolidone (NMP) as a cosolvent. Subsequently, the prepolymer is chain extended to high molecular weight by the addition of highly reactive diamines which diffuse through the aqueous phase to the dispersed prepolymer particles. The prepolymer process has barriers to making well-defined and characterized structures due to the reactive prepolymer intermediate and having the chain extension step performed in heterogeneous environment with diffusion control over one of the reactant concentrations.

Processes have been for the preparation of dispersions in which dispersion step takes place after completing the polymerization in homogeneous solution.[22−32] This process, hereinafter referred to as the "acetone process", uses a low boiling point water miscible organic solvent, such as acetone or methylethyl ketone, to carry out the polymerization in a concentrated solution. After dispersion of polymer solution into water the solvent is recovered for reuse by distillation. Though practiced industrially,[33−35] there are few published studies describing this process in the open literature.[36−42] The advantages of this route are readily apparent, as the finished polymer is prepared in a highly controlled fashion with characterization and adjustments possible before dispersing. An additional benefit comes from having the low boiling solvent completely removed by distillation after the dispersion, yielding a product containing little or no volatile organic content.

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In this contribution we report on using the latter route to prepare polyurethane−polyhedral oligomeric silsesquioxane (PU−POSS) hybrid dispersions through homogeneous polymerization with acetone as the reaction solvent. With the removal of acetone after addition of the water, virtually organic solvent free products were obtained. Films prepared from these dispersions did not display phase heterogeneity, and significant change in physical properties were found compared to the unmodified PU base formulation.

Experimental Section

Materials. Poly(hexylene adipate−isophthalate) polyester diol (Desmophen 1019-55−OH# 55 and Acid# 2) and isophorone diisocyanate (IPDI) (Desmodur-I) were supplied by Bayer Material Science, Pittsburgh, PA. Dimethylolpropionic acid (DMPA), dibutyltin dilaurate (DBTDL), triethylamine (TEA), and 1,4-butanediol (BD) were received from Aldrich Chemical Co. Acetone (99.5%) was received from Fluka. 3-(2-Aminoethyl)amino)propyl-heptaisobutyl-POSS (diamino-POSS) and 2,3-propanediol propoxy-heptaisobutyl-POSS (diol POSS) were provided by Hybrid Plastics, Hattiesburg, MS. All materials were used as received.

Films used for dynamic mechanical analysis (DMA), rheology studies, WAXD, and mechanical testing were prepared by casting onto a polypropylene plate and drying in a vacuum oven at 120 °C for 3 days. Solutions for gel permeation chromatography (GPC) analysis were prepared by dissolving a small amount of the dried film in tetrahydrofuran (THF). Samples for contact angle measurements were prepared by applying the films at 5 mills using a bar-coater on well-cleaned glass substrates, followed by air-drying for 20 h at ambient temperature and oven drying at 50 °C for 4 h. The wt % of the solids in the formulation was verified by heating 1 g of dispersion in a glass vial in a vacuum oven at 120 °C for 6 h and measuring the retained mass.

Measurements. Dispersion particle sizes and distribution (PS) were determined by dynamic light scattering performed on a Microtrac UPA 250 ultrafine particle analyzer. The samples were diluted to the required concentration with distilled water before measurement. The analysis was carried out with estimated solution parameters as follows: refractive index of 1.81, particle density of 1.0 g/mL, and viscosity between 0.797 and 1.002 mPa·s. The time for each analysis was fixed at 360 s, and a minimum of two analyses were performed verify reproducibility.

GPC measurements in THF were performed using a Polymer Laboratories model PL-ELS 1000 using a PLgel 5 μm MIXED-C, 300 × 7.5 mm column and a Waters 590 HPLC pump at a flow rate of 1 mL/min. The GPC was calibrated with monodisperse poly(methyl methacrylate) (PMMA) standards with PDIs < 1.04. Nine different PMMA standards of $M_n = 1000, 1800, 6500, 14\,000, 30\,000, 62\,000, 148\,000, 242\,000$, and $550\,000$ were used to the calibration curve.

WAXD experiments were carried out on POSS powder and on 500 μm thick PU films with a Rigaku Ultima III rotating anode X-ray generator operating at 40 kV and 250 mA with a Cu target and graphite monochromator. The scanning was performed at $2\theta = 2°-40°$ with step size of 0.02° and 4 s per step.

DMA of the films prepared from the dispersions was carried out using a TA Instruments DMA 2980 dynamic mechanical analyzer in the tensile mode. The temperature response was calibrated with indium while the force and compliance calibrations were performed using standard weight and a clamped steel bar, respectively. Films of 0.80 × 4.80 × 12.8 mm were used for the DMA testing, and the viscoelastic properties were measured under a nitrogen atmosphere, at a heating rate of 2 °C/min from −100 to 150 °C and a frequency of 10 Hz. The measurements were performed in triplicate, and the average was reported.

Tensile stress−strain measurements were obtained from the film samples (thickness of ∼0.8 mm and a width of ∼3.2 mm) using a stnadard Instron 4502 following ASTM standard E111 (1997) method. The cross-head speed was set at 2 mm/min, and the test continued until sample failure. A minimum of three tests were analyzed for each sample, and the average values are reported.

Surface topography was characterized by atomic force microscopy (AFM) in tapping mode using silicon tips (scan area 625 μm^2) with a Dimension 3000 AFM (atomic force microscope) with NanoScope IIIa controller from Veeco. Samples were prepared on silicon wafer surfaces by air-drying 5 wt % dichloromethane solutions of polymer from films prepared as above.

Solution viscosity was measured at 25 °C using a Brookfield DV-I viscometer with a no. 2 spindle at a shear rate of 100 s^{-1}. Viscoelastic measurements on the films were performed using an Advanced Rheometrics Expansion System (ARES, Rheometrics Inc.) equipped with 25 mm parallel plates. Strain sweeps were carried out at a constant temperature (110 °C) over a frequency range of 0.1−100 rad/s to determine the linear viscoelastic range of the samples. Frequency sweeps were performed at variable temperatures (100−130 °C) in the linear viscoelastic region (i.e., strain amplitude ≤ 10% strain) to construct master curves for the modulus (G') for different PU−POSS compositions.

Contact angles were determined using a Dataphysics OCA 20 contact angle meter employing distilled, deionized water as the reference liquid. About 10 independent measurements were carried out, and the average contact angle was reported.

Representative PU−POSS Hybrid Synthesis (PU10). In a 500 mL round-bottom flask equipped with a nitrogen bubbler, 10.0 g of diamino-POSS (0.021 amine equiv) was dissolved into 125 g of acetone. To this solution 23.0 g of IPDI (0.207 isocyanate equiv) was added dropwise while stirring using a magnetic stirrer at 20 °C. After 20 min, 3 drops of DBTDL were added. After 10 min the flask was fitted with a mechanical stirrer, a thermocouple controlled heating mantel, a condenser with nitrogen bubbler, and a pipet outlet. The polyester polyol (61.1 g, 0.06 hydroxyl equiv) and DMPA (3.1 g, 0.046 hydroxyl equiv, 0.023 acid equiv) were charged into the flask, and stirring was continued while the temperature was raised to 60 °C. The isocyanate (NCO) content was monitored during the reaction using the standard dibutylamine back-titration method.[42] Upon reaching the theoretical NCO value, the prepolymer was chain extended with BD (2.6 g, 0.057 hydroxyl equiv), and the reaction continued for 2 h to complete polymerization, yielding the desired polyurethane/POSS copolymer. Last, the polymer was neutralized by the addition of 2.3 g of triethylamine (0.023 equiv) and stirred for 30 min while maintaining the temperature at 55 °C. Formation of the dispersion was accomplished by slowly adding 212 g of water to the neutralized acetone solution of the polyurethane polymers at 45−50 °C over 30 min with an agitation speed of 600 rpm. After stirring for 30 min, the reaction mixture was transferred to a rotary evaporator, and the acetone was removed at 35 °C and a partial vacuum of 70 mmHg to afford organic solvent free dispersions with 32 wt % solids.

PU Control Dispersion Synthesis (PU0). PU sample preparation without POSS was carried out in a 500 mL round-bottom, four-necked flask with a mechanical stirrer, thermocouple, a condenser equipped with a nitrogen bubbler, and a pipet outlet. To the reactor, 73.3 g of the polyester diol (0.071 hydroxyl equiv) and 3.1 g of DMPA (0.046 hydroxyl equiv, 0.023 acid equiv) were charged. While mixing, 85 g of acetone was added, and stirring was continued until a homogeneous mixture was obtained. IPDI (21.2 g, 0.19 isocyanate equiv) and 3 drops of DBTDL were added dropwise with continued stirring at 60 °C. Upon reaching the theoretical NCO value, the prepolymer was chain extended with BD (2.4 g, 0.053 hydroxyl equiv), and the reaction was allowed to continue for 2 h to finish the polymerization. The final polymer was neutralized by the addition of 2.3 g of triethylamine (0.023 equiv) and stirred for 30 min while maintaining the temperature at 55 °C. The dispersion was accomplished as detailed for **PU10**.

Results and Discussion

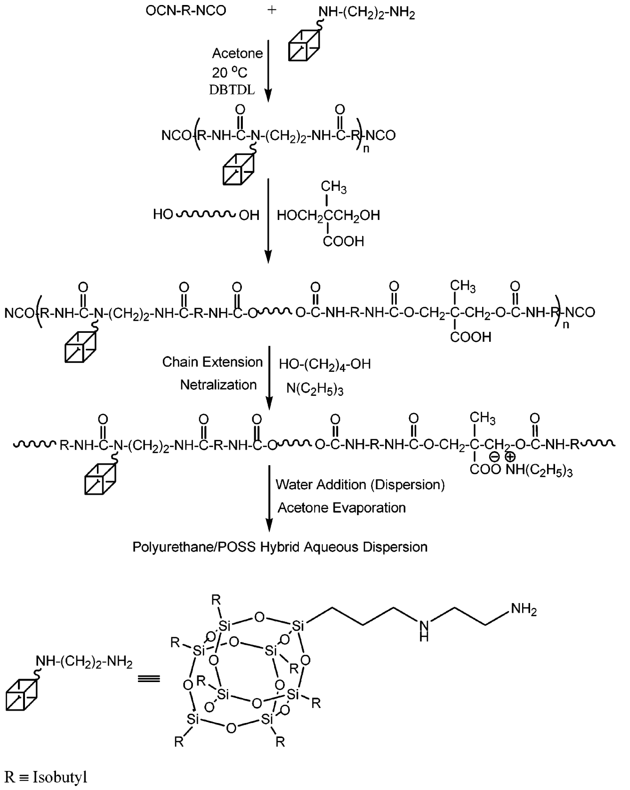
The acetone process used in the preparation of PU dispersions was evaluated for the formation of PU−POSS hybrids with POSS contents on total polymer solids of 4, 6, and 10 wt %

Table 1. PU−POSS Hybrid Compositions

sample[a]	POSS wt (equiv)	IPDI wt (equiv)	polyester diol wt (equiv)	DMPA wt (equiv)	BD wt (equiv)
PU0	0 (0)	21.2 (0.190)	73.3 (0.071)	3.1 (0.046)	2.4 (0.053)
PU4	4.0 (0.009)	21.7 (0.196)	68.5 (0.067)	3.1 (0.046)	2.4 (0.053)
PU6	6.0 (0.013)	22.2 (0.199)	66.1 (0.064)	3.1 (0.046)	2.5 (0.055)
PU10	10.0 (0.021)	23.0 (0.207)	61.1 (0.060)	3.1 (0.046)	2.6 (0.057)
PU10A	10.0 (0.021)	22.9 (0.206)	61.2 (0.060)	3.1 (0.046)	2.6 (0.057)

[a] **PU4**−**PU10**: diamino-POSS. **PU10A**: diol-POSS.

Scheme 1. Elementary Steps for the Synthesis of the PU−POSS Hybrid Dispersions and an Idealized Structure of the Diamino-POSS



(**PU4**, **PU6**, and **PU10**, respectively). The reactant charges for the dispersions are given Table 1 along with those for the control dispersion (**PU0**) and an additional dispersion prepared using 10 wt % of a diol POSS monomer (**PU10A**). For all of the samples the following variables were held constant: [DMPA] at 3 wt % based on total concentration of polymer, [polymer] at 32 wt %, and chain extension at 90%. To compensate for the inclusion of the POSS monomers, the polyester diol content was reduced from 73 to 62 wt % of the total polymer solids as the [POSS] was varied from 0 to 10 wt %. In the process reported here (Scheme 1), the diamino-POSS was first dissolved in acetone, before reaction with IPDI. Subsequent steps of prepolymer formation, chain extension, and neutralization were unchanged from the method used for non-POSS-containing control dispersion (**PU0**). Carrying out the first step of the synthesis in acetone was found to be essential for obtaining a homogeneous reaction mixture as the urea formed was found precipitate in the absence of acetone.

The inclusion of the POSS monomers did not have a major impact on the dispersion properties of the dispersions relative to the control (**PU0**). The minor differences in particle size and viscosity with increasing POSS content are within the limits of reproducibility and indicate that the POSS monomers do not affect the dispersion step (Table 2). The dispersion particle sizes for all samples were unimodal and remained constant over 6 months of storage at room temperature (Figure 1).

Table 2. Particle Size and Viscosity of the PU−POSS Hybrid Dispersions

sample	particle size (nm)	η (mPa·s)
PU0	107	77
PU4	109	75
PU6	111	74
PU10	112	73
PU10A	113	75

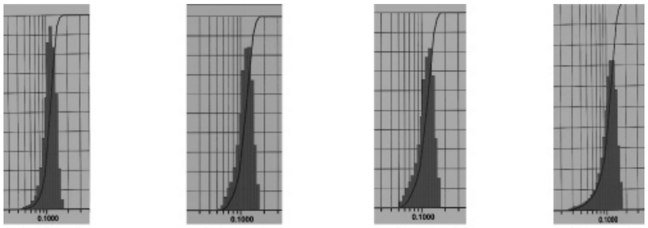

(113 nm) 1 day (115 nm) 1 month (115 nm) 3 months (115 nm) 6 months

Figure 1. Particle sizes of **PU10** during storage.

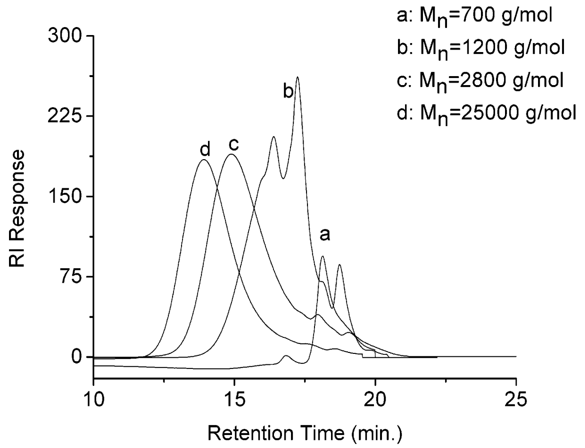


Figure 2. GPC chromatograms of (a) diamino-POSS, (b) diamino-POSS + IPDI, (c) prepolymer, and (d) final polymer of **PU10**.

The reaction mixtures were analyzed at each step of the sequence to verify that the comonomer was incorporated. Figure 2 shows the GPC traces of the diamino-POSS monomer and the three steps of polymerization prior to neutralization. The molecular weights determined by GPC, though not absolute, are useful to qualitatively follow the increase in molecular weight at different stages of the polymerization. These clearly show that the vast majority of the diamino-POSS is incorporated on the first step and that the final polymer is virtually free of residual POSS comonomer ($M_n \sim 700$ g/mol).

Determining the phase segregation behavior of the POSS residues in films prepared from these dispersions is critical to the understanding the relationship between POSS content and the resulting physical properties. In general, films prepared from aqueous polyurethane dispersions do not exhibit the clear formation of crystalline hard segment domains that are found in many polyurethane elastomers or plastics. The chemistry of the products and the need to coalesce into a continuous film precludes the high level of crystallinity that is found in the melt

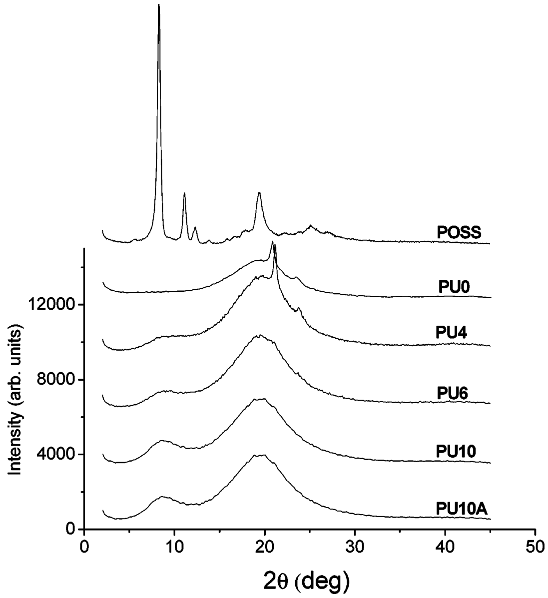


Figure 3. WAXD patterns of the PU−POSS hybrids, diamino-POSS, and **PU0** (control).

or solvent processes polyurethanes. The presence of the hard segment domains is inferred from a higher temperature change in physical properties (softening point) that is not accompanied by a detectable thermal transition in DSC measurements.

Depending on which phase the POSS residues partition to, inclusion of the POSS monomers could affect film visual properties (clarity, etc.), morphology, and physical properties. As a first indicator of film heterogeneity film clarity is tied to the absence of macrophase separation and would be expected to drop if large POSS-rich domains are being formed in the solid state. All of the films prepared from these dispersions were clear and defect free, but additional analysis is required to indentify changes on the microscopic scale.

Further evidence of the homogeneity comes from wide-angle X-ray analysis of the films (Figure 3). The X-ray pattern for the control sample (**PU0)** showed a sharp small reflection at $2\theta = 20.9°$ superimposed on a broad amorphous halo centered at $2\theta = 19.5°$ from the polyurethane hard segment. With the inclusion of 4 wt % POSS (**PU4**), the sharp peak and broad reflection for PU is still present with an additional broad peak at $2\theta = 8.6°$. For samples **PU6** and **PU10** the sharp reflection found in **PU0** completely disappears, leaving the two amorphous halos centered at $2\theta = 8.6°$ and 19.5° as the only features seen in the X-ray pattern.

The X-ray pattern (also given in Figure 3) obtained for the unreacted diamino-POSS monomer has well-defined reflections found at $2\theta = 8.1°$, 10.8°, 12.1°, and 18.8°, similar to those reported for the TMP-diolisobutyl-POSS by Turi.[21] These sharp reflections corresponding to the crystalline monomeric POSS were not detected in any of the films prepared from **PU4**−**PU10**. The amorphous halo centered at 8.6° indicates that the presence POSS residues either is causing some type of additional order or is more likely increasing the volume of the hard segment phase into which it partitions.

Though WAXD characterization may not sensitive enough to preclude the presence of a separate POSS-rich crystalline phase if the composite produces small crystal size, it does allow the conclusion that these samples do not have the same crystal structure reported for the earlier PU−POSS work. The films characterized by Turi had sharp crystalline reflections POSS clearly visible at $2\theta = 8.1°$ in the WAXD pattern.[21]

Table 3. Physical Properties of the PU−POSS Hybrid Films

			at break	
sample	contact angle (deg)	hard segment softening point (°C)	tensile strength (N/cm^2)	elongation (%)
PU0	64.1 ± 2	53	60	2000
PU4	82.0 ± 2	56	102	1200
PU6	85.0 ± 2	66	210	1100
PU10	89.0 ± 2	90	625	900
PU10A	88.4 ± 2	91	620	900

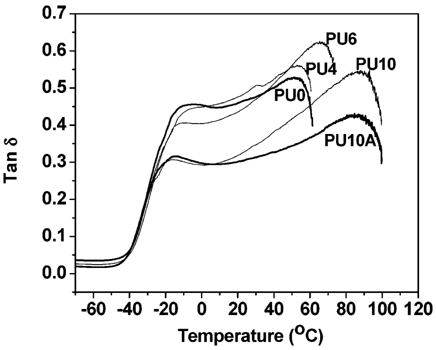


Figure 4. Tan δ vs temperature of the PU−POSS hybrid films.

Physical properties may be the best way to track changes resulting from the inclusion of the POSS monomers into polyurethane dispersions. Changes in thermal behavior vs the control give insight on the molecular scale, while changes in film modulus reflect both molecular and larger scale morphological changes. For the materials discussed here, with a very soft base formulation, any partitioning of the POSS residues into the soft segment phase would result in a large increase of the soft segment T_g. Partitioning into the hard segment phase could lead to an increase in softening temperature based on either increased integrity or through an increase in the volume fraction of the hard segment. An increase in the volume fraction of the hard segment would also have a predictable impact on modulus above the glass temperature of the soft segment. Partitioning to form its own phase, separate from those already found in the polyurethane, would be readily observable as a new thermal transition in DMA or DSC.

Initial tensile tests on films prepared from the series revealed major changes based on the inclusion of POSS (Table 3). The physical properties changed systematically with POSS content as evidenced by tensile strength at break increasing by a factor of 10, from 60 N/cm^2 for the control (**PU0)** up to more than 600 N/cm^2 for the samples containing 10% of the POSS monomers (**PU10**, **PU10A**). Concurrently, there is an expected drop in elongation at break, though the stiffest films with 10% POSS still attained 900% elongation before breaking.

The differences in physical properties induced by the inclusion of POSS are also apparent from the results obtained from DMA testing (Figures 4 and 5). At lower temperature, E' increases moderately with POSS content, with the major impact being seen at higher temperatures. The plots of tan δ for the polymer series show no significant variation in the lower temperature maximum between −15 and −20 °C arising from the soft segment T_g as the amount of POSS is increased. In the higher temperature range where one finds the hard segment softening point, there is a large change with the tan δ maximum rising incrementally from 53 to 90 °C as the amount of POSS is increased.

These results suggest that the POSS moieties are incorporated in the hard segments rather than with soft segments. The noted

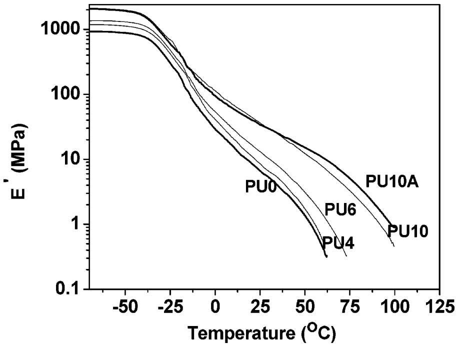


Figure 5. E' vs temperature of the PU−POSS hybrid films.

Table 4. Calculated Weight Percent of the "Hard Segment" Content for POSS Partitioning into Soft Segment or Hard Segment Phases

	POSS in soft segment	POSS in hard segment
PU0	17	17
PU4	17	22
PU6	17	24
PU10	17	30
PU10A	17	30

changes in physical properties fall in line with those expected with an increase in hard segment content of a polyurethane and are in line with first-order estimates of hard segment content as the amount of POSS is increased. The estimates for this polymer series provided in Table 4 were made assuming that the "hard segment" content of the control polyurethane (**PU0**) is comprised of the butanediol, DMPA, and the molar equivalents of isocyanate they react with. If the functionalized POSS reaction products partition into the soft segment domains, there would be no change in hard segment domain content. With partitioning into the polyurethane-rich hard segment phase there would be an overall increase in hard segment content from 17 to 30 wt % (Table 4) as the POSS level was increased to 10% of total composition.

While rheology is not the focus of the present paper, it is well know that shear rheological properties are important in understanding the morphology development of hybrid dispersions and films such as the present PU/POSS hybrid systems. Therefore, extensive rheological measurements and analysis over a wide range of temperatures including the microphase separation temperature will be reported in our next publication. However, the above DMA results show that POSS strongly impacted the rheological behavior of PU films (Figure 6a). At equivalent POSS loading both the diol-POSS-derived dispersion (**PU10A**) and that of the amino-POSS (**PU10**) had comparable rheology (Figure 6a). Similar behavior has been observed for the master curves of the same materials as shown in Figure 6b. The thermorheological simplicity rule is valid only over a narrow range of temperature (100, 110, 120, and 130 °C). At temperature higher than 130 °C the time−temperature superposition principle is no longer valid due to the microphase separation of the hard and soft segments or due to what is called order−disorder transition of the two different segments of PU main chain.[43]

The dependence of dynamic viscosity on POSS concentrations for the PU−POSS films at different shear frequencies is displayed in Figure 7. The incorporation of POSS into the PU backbone produced a significant change in the dynamic viscosity. At 110 °C, the viscosity increases linearly with [POSS], corroborating the reinforcing efficiency of POSS in the PU backbone. The dynamic viscosity strongly depends on frequency (Figure 7), revealing the non-Newtonian behavior of PU−POSS composites in which the dynamic viscosity at low frequencies is significantly higher than that obtained at high frequencies.

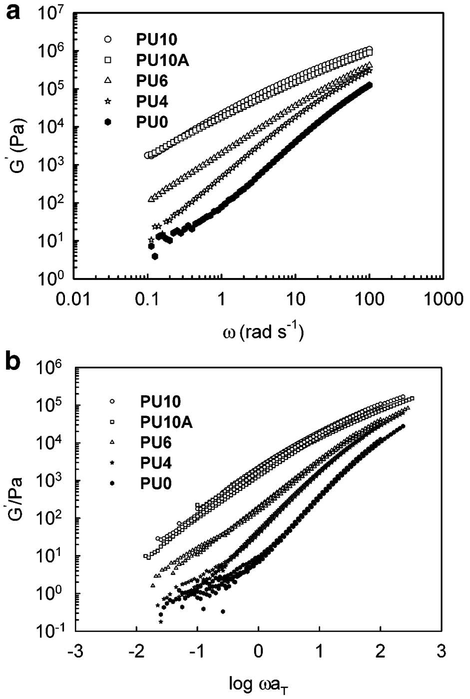


Figure 6. (a) Elastic modulus of the PU−POSS hybrid films at 110 °C with variable frequencies. (b) Master curves for different PU−POSS composites at T = 110 °C reference temperature.

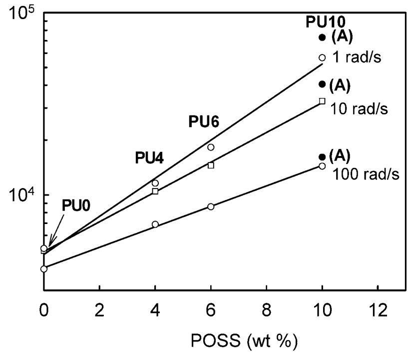


Figure 7. Effect of POSS content on melt viscosity of the PU−POSS hybrids at 110 °C.

The results we have reported so far apparently show the homogeneous incorporation of POSS into the PU matrix. However, a significant impact on the morphology is seen in surface tension measurements taken on films cast from aqueous solution. Incorporation of the POSS comonomers had a major impact on the film surfaces as evidenced by the large change in water contact angle reported in Table 3. Incorporating 4 wt % POSS (**PU4**) results in an increase the contact angle from 66° to 82°, and higher loadings slowly increase the contact angle to 89°. This phenomenon is quite commonly observed for POSS modified polymers with as surface tension preferentially drives the lower energy POSS residues to the air interface.[44,45]

AFM measurements were performed to identify changes in surface morphology related to the drop in surface tension. Films prepared from the aqueous solution were basically featureless, not showing any specific surface morphology or topology related to hard blocks or soft block separation. However, a major impact on the morphology was found when the films were recast from organic solution. The AFM images in Figure 8 were obtained for samples of the **PU0** and **PU10** samples recast from CH_2Cl_2 as an attempt to get thinner/smoother films than were initially

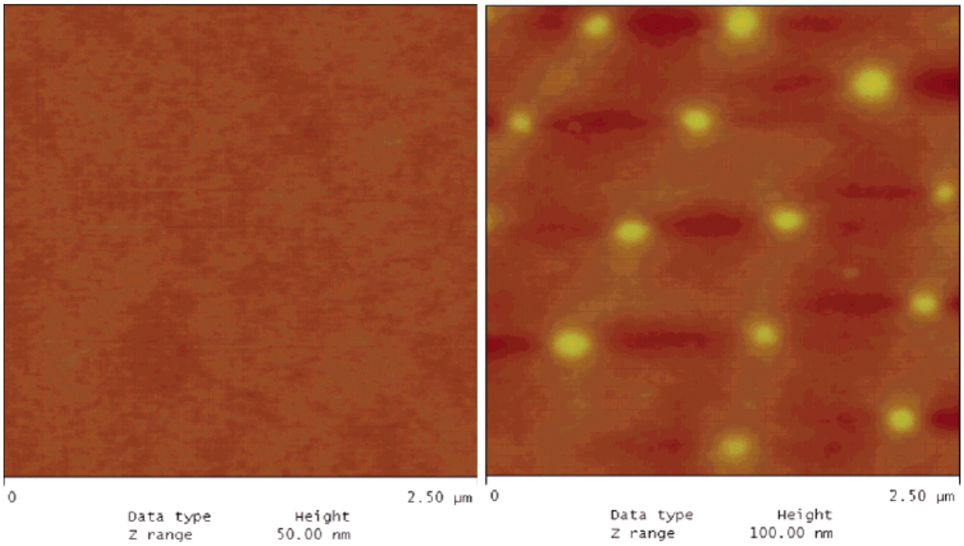


Figure 8. AFM topography images of solvent cast **PU0** (left) and **PU10** (right) samples.

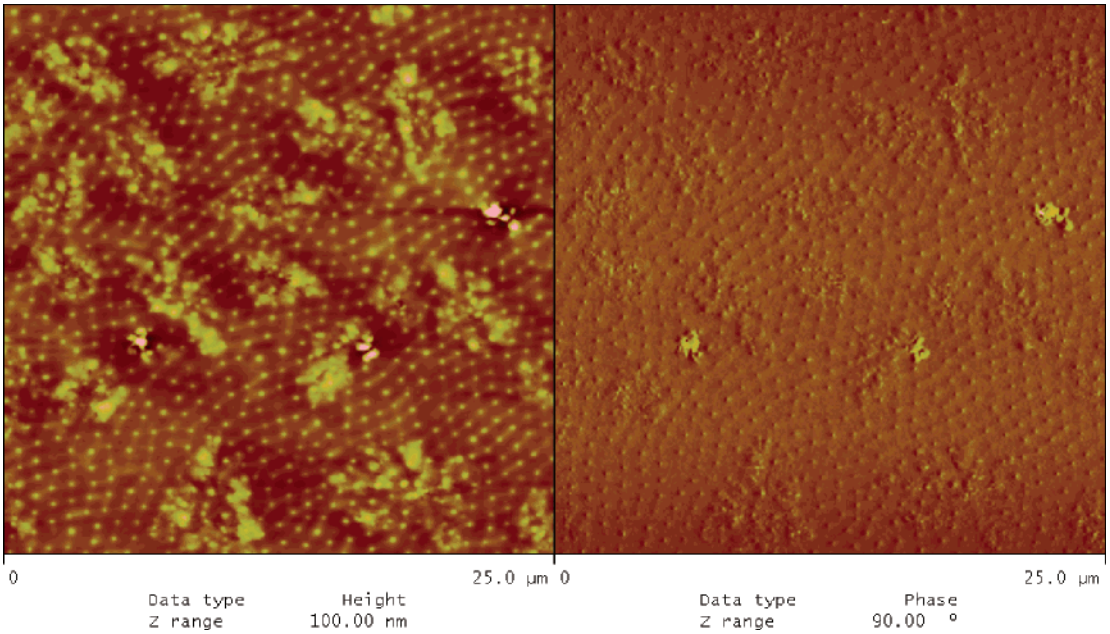


Figure 9. Expanded AFM height and phase images of **PU10**.

attained from aqueous solution. The **PU0** film presented a featureless surface (Figure 8, left) similar to those obtained for the original films cast from water. The result was drastically different for the recast films prepared from the POSS-containing materials which were found to have an ordered morphology. As an example of this, the image for the **PU10** sample (Figure 8, right) reveals the presence of regularly placed domains in a trapezoidal configuration. The order extends over a large range (Figure 9) with the domains showing an increased height (Figure 9, left) and higher phase hardness (Figure 9, right). These domains which appear to due to the presence of POSS have an average size of 100−120 nm and a spacing of 600−900 nm. Though the morphology changes are the subject of ongoing studies, it appears that the strong organic solvent facilitates the POSS-containing segments to aggregate. With the original dispersions at the time of film formation there is no organic solvent which may limit the mobility of the hard segments. The restricted mobility, which with a very low T_g soft segment does not inhibit coalescence, could inhibit an aggregation process for the containing urethane−POSS residues.

Conclusions

It has been shown that waterborne polyurethane hybrid dispersions have been successfully synthesized by incorporating amino- and hydroxy-functionalized POSS macromers into polyurethane ionomeric backbones using homogeneous solution polymerization followed by solvent exchange with water (i.e., the “acetone process”). All the compositions of the PU−POSS dispersions studied are stable for more than 6 months, and their low level of volatile organic compounds (i.e., VOC < 1%) shows the advantages of the acetone process over the prepolymer method. The POSS macromers appear to be included in the PU hard segments as evidenced by the absence of crystalline domains and the steady increase in hard segment softening point with increased POSS content.

Our results are in contrast to those reported by Turi and Levi,[21] indicating the strong sensitivity of small variations in process and composition on the properties of the PU−POSS films. Overall, the results of this study show unambiguously that the sequencing of the reaction steps at the outset of polymer preparation dictate whether the POSS is homogeneously incorporated, making it possible to prepare nanostructured PU−POSS films with desirable morphology and physical properties.

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