

FLUOROPOLYMER PROPERTY ENHANCEMENT VIA INCORPORATION OF FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUOXANES (FLUOROPOSS)

Joseph M. Mabry,^{1*} Darrell Marchant,¹ Brent D. Viers,²
Patrick N. Ruth,¹ Scott Barker,² and Constance E. Schlaefel²

¹ERC, Inc., Air Force Research Laboratory, Edwards AFB, CA 93524

²Air Force Research Laboratory, Edwards AFB, CA 93524

ABSTRACT

Fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS) are the newest class of POSS compounds. These compounds have the highest molecular weights and highest densities of any POSS compounds yet produced. They also have remarkable surface properties, which have been observed in water contact angle measurements. A number of FluoroPOSS compounds have been produced from their respective trifunctional monomers. These FluoroPOSS compounds have been blended into several fluoropolymers, including fluorinated ethylene-propylene (FEP), poly(chlorotrifluoroethylene) (PCTFE), and poly(vinylidene fluoride) (PVdF). The POSS blendables appear to be well dispersed in scanning electron microscopy (SEM) and atomic force microscopy (AFM) spectra. These POSS fluoropolymers may be useful as low friction surfaces or hydrophobic coatings. Contact angle measurements of the POSS fluoropolymers show an improvement in water contact angles over the unfilled materials. The low surface energy POSS compounds also appear to act as a processing aid during fluoropolymer processing, significantly reducing both the torque and load measurements in the extruder. Thermal and mechanical properties of the blended fluoropolymers do not differ significantly from those of the unfilled polymers.

KEY WORDS: Nanocomposites, POSS, Fluoropolymer

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1. INTRODUCTION

The field of polyhedral oligomeric silsesquioxanes (POSS) continues to expand as new types of compounds are explored for use in many applications (1). These applications include space-survivable coatings (2-4), and ablative and fire-resistant materials (5-7). POSS compounds have a rigid, inorganic core and have been produced with a wide range of organic functionality. POSS can be produced as either completely condensed cages or incompletely condensed cages with silanol groups that allow further modification. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, often improving both thermal and mechanical properties.

The addition of fillers to polymeric matrices is of extreme technological importance. However, the effects of this process are still not fully understood. Filler addition can impart enhanced scratch resistance, increase thermal or mechanical properties, and improve processing parameters. There has been much effort to optimize the factors in the addition of filler. One factor is filler chemistry. Silicate and carbon black based fillers are quite common. They are often inexpensive and their incorporation into many polymer systems is fairly straightforward. When miscibility is a problem, surface modification of the fillers to further enhance their compatibility is widespread. The silylation of surface silanol groups on silica fillers is a good example. Processing is another factor that has been optimized. The use of high shear to break up large agglomerates or aggregates of nanoscopic particles is common. These approaches yield nanoscopic species with large surface areas, which should favor physisorption and/or chemisorption between the polymer chain and the filler.

A number of recent reports have detailed that POSS materials can act as reinforcing fillers (or reinforcing comonomers) in a number of nanocomposite systems (8-10). The results reported herein are somewhat different in that the monodisperse POSS building blocks seem to be rather non-interacting. Specifically, the organic "corona" surrounding the silsesquioxane core is composed of fluoroalkyl moieties. Fluoroalkyl compounds are known to be basically inert. This is largely because they are non-polarizable and have low surface free energies. Fluoroalkyl chains are often rigid, due to steric and electronic repulsion. Similarly, the large corona of the FluoroPOSS compounds should retard the van der Waals attraction between POSS cores. These POSS materials are monodisperse and crystalline. The melting point of the POSS is lower than the processing conditions of the fluoropolymers, so one can safely assume that hard filler effects should not be an issue. In this regard, one may expect that these materials could exhibit small molecule, solvent like, characteristics. The POSS could be well dispersed and act as a molecular ball bearing. This paper will discuss many of the parameters and physical properties of simple blends of FluoroPOSS materials in fluoropolymer matrices. It will be demonstrated that these simple blends do not rigorously correspond to idealized filled polymer models or to solvent swollen systems. Herein, we describe the properties resulting from the blending of these new POSS compounds into various fluoropolymers.

2. EXPERIMENTAL

2.1 Materials POSS compounds, 1H,1H,2H,2H-heptafluorodecyl₈T₈ (Fluorodecyl POSS), 1H,1H,2H,2H-tridecafluorooctyl₈T₈ (Fluorooctyl POSS), and 3,3,3-trifluoropropyl_nT_n (Fluoropropyl POSS) were prepared using previously reported methods (11). Fluorinated ethylene/propylene (FEP T-100) was generously donated by DuPont Fluoroproducts in Parkersburg, West Virginia. Polychlorotrifluoroethylene (PCTFE or Neoflon M 400-H) was obtained from Daikin. Polyvinylidene fluoride (PVdF or Hylar 460) was purchased from Solvay Solexis.

2.2 Composite Preparation Fluoropolymer composites are prepared by adding five, ten, or fifteen weight percent of fluorodecyl and fluoroctyl POSS melt blended into FEP and PCTFE. All samples were blended in a DACA Micro Compounder for 3 minutes at 100 rotations per minute. The DACA Micro Compounder is a conical co-rotating twin-screw extruder with a bypass allowing the material to circulate for specified times. The capacity of the mixer is 4.5 cm³. The mean shear rate is approximately 100 s⁻¹ and is reported based on a treatment given in literature (12). The blends were compounded at 280 °C. Furthermore, samples of ten weight percent of Fluoropropyl and Fluoroctyl POSS were blended into PVDF at 177 °C for compatibility studies. Samples for dynamic mechanical thermal analysis (DMTA), contact angle measurements, and atomic force microscopy (AFM) were thin films. Samples for scanning electron microscopy (SEM) were 1/8 in thick bars. The films were made by compression molding two grams of the polymer-blend extrudate utilizing a Tetrahedron compression molder. The polymer extrudate was placed between two sheets of thick aluminum foil at 10 °C greater than the compounding temperatures for 10 minutes using one ton of force. All films were less than 0.3 mm thick and about 80 mm in diameter and appeared homogenous and similar to the respective unfilled fluoropolymer. The bars for SEM were also compression molded with the same molding times and temperatures, but utilizing only ½ ton of force.

2.3 Thermo-mechanical Analysis The compression molded films were cut into 3 x 20 mm rectangular samples for dynamic mechanical thermal analysis utilizing a DMTA V from TA Instruments. All fluoropolymer samples were analyzed using a 5°C temperature ramp and a tensile geometry. The FEP and PCTFE samples were each tested from 30 °C to 150 °C. Stress/strain tests were performed on all samples to identify the largest force in which the material exhibited an elastic deformation, thus limiting the pre-tension force used to test the samples. Strain sweeps were also performed to ensure that the testing strain is within the linear viscoelastic region. The FluoroPOSS effect on the thermal stability of the fluoropolymers was examined using a 2050 TGA from Rheometric Scientific in the presence of nitrogen.

2.4 Microscopy The dispersion of the FluoroPOSS was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2.4.1 Atomic Force Microscopy (AFM) The AFM measurements were performed in tapping mode by a Digital Instruments Dimension 3100 Scanning Probe Microscope (SPM), which utilizes automated atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques. Atomic Force Microscopy was conducted on a Nanoscope IV controller (3100 SPM Head) in tapping mode. Etched Silicon probes of nominal spring resonance 300 kHz (spring

constant approx. 0.3 mN/m) were used for light tapping (driving amplitude ca 1.1 V) of varying section size at 1-2 Hz collection times (512 points/line). Both the surface topography (height) and phase imaging (indicative of surface mechanical properties) were collected. The AFM samples are cut from the compression molded films discussed in the results and discussion section. It was noted that most of the surfaces did not have a significant phase image, which was interpreted as being indicative of relatively uniform surfaces that differed only in surface topography. The surface roughness was dominated by the processing effects, e.g. gross striations indicative of film buckling upon removal. However, fine scale features were resolvable and will be discussed. In the AFM micrograph images, height will be shown on the left side of the figure and a simultaneously collected phase image will be shown on the right.

2.4.2 Scanning Electron Microscopy (SEM) Scanning electron microscopy was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector. Elemental mapping was performed using energy dissipation X-ray analysis with IXRF Systems analysis software. Samples were cut from compression molded bars and the cross-section was imaged. Furthermore, an elemental mapping of the surface is discussed.

2.5 Contact Angle Contact Angle analyses were performed on a First Ten Angstroms 110 series system using a syringe metering pump. Deionized water (18 M Ω ·cm, Barnstead) was used as the interrogating liquid. Small drops of water (approximately 2-5 μ l) were accurately metered onto a flat surface, and the full screen image of the drop was captured with the frame grabbing software coupled to a CCD camera operating at the optimized zoom and contrast. The contact angle was determined via the software suite (fit to a sphere/pseudosphere with a baseline entered for the liquid-solid contact line) or via graphical fitting of the contact tangents in the captured image. Both approaches gave the same nominal value within ± 2 degrees. Only the value of the quasistatic advancing angle is reported. An analysis of the advancing and receding behavior will be the subject of future work.

3. RESULTS AND DISCUSSION

3.1 FluoroPOSS Synthesis FluoroPOSS were produced by the base-catalyzed hydrolysis of trialkoxy silanes. These compounds tend to condense into T₈ cages, rather than cage mixtures, as has been previously observed in the base-catalyzed synthesis (Figure 1). This is significant because the usual method to produce T₈ cages is the acid-catalyzed hydrolysis of trichlorosilanes, which produces an undesirable acidic byproduct.

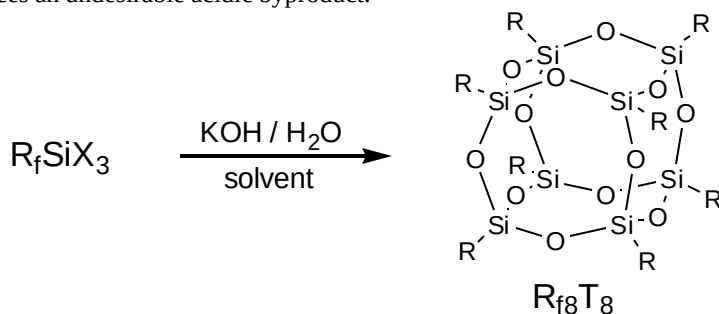


Figure 1. Synthesis of Fluoroalkyl₈T₈.

The synthesis of Fluoropropyl_nT_n, producing a mixture of isomers consisting mainly of T₁₀ and T₁₂, was previously known. This isomeric mixture is typical of the base catalyzed POSS synthesis (Figure 2).

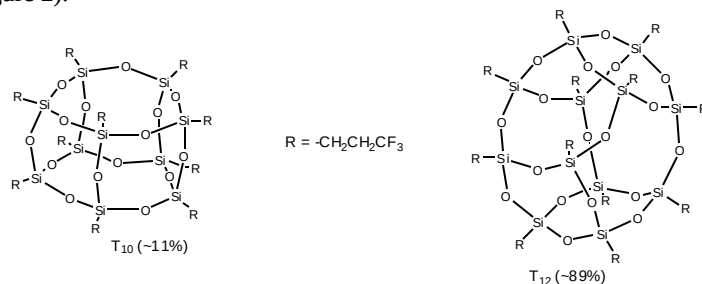


Figure 2. Fluoropropyl T₁₀ and T₁₂ cages.

A variety of fluoroalkyl POSS compounds have been produced, including fluorodecyl, fluoro-octyl, and fluoropropyl. Synthesis is currently underway on a number of others. The yields for these reactions are often nearly quantitative, but may be as low as 75%. The byproduct is a resinous material that is formed when the condensation is less controlled. The resin is typically removed by extraction.

3.2 FluoroPOSS Properties The properties of the FluoroPOSS compounds are quite interesting. They tend to volatilize at approximately 300 °C, rather than decompose, as is observed with many POSS compounds. The FluoroPOSS are the highest molecular weight POSS yet produced. The Fluorodecyl POSS has a molecular weight of 3993.54 g/mol. The density of these materials is also very high, with crystals of the Fluorodecyl POSS having a density of 2.058 g/mL.

Various surface properties of the FluoroPOSS compounds have been examined. Water contact angles are a measure of the surface free energy of a surface. As the surface energy decreases, the contact angle increases to a maximum of 180°. The trend observed in the FluoroPOSS compounds is that the surface energy decreases as the length of the fluoroalkyl chain increases. While this may not be surprising, the observed contact angles are unexpectedly high. The Fluorodecyl POSS has a water contact angle of over 150°, which is approximately 40° higher than the water contact angle of PTFE. The correlation between the chain length and the contact angle is not linear. The contact angle appears to be increasing at an increasing rate.

3.2 POSS Fluoropolymers The FluoroPOSS compounds mentioned above were blended into several different fluoropolymers. For the purposes of this paper, Fluoropropyl and Fluorooctyl POSS/PVdF blends will be used to describe dispersion results. Fluorooctyl and Fluorodecyl POSS blends in FEP and PCTFE will be used to describe processing, thermo-mechanical and surface properties.

3.2.1 Dispersion The level of dispersion of POSS compounds into polymer systems is largely dependent on surface chemistry. A good example is the blending of POSS into poly-vinylidene fluoride (PVdF). PVdF has a -CH₂CF₂- repeat unit. Therefore, the fluorine to

hydrogen (F/H) ratio is 2/2. The Fluoropropyl POSS has a F/H of 3/4, which is very similar to that of PVdF. Fluorooctyl POSS, on the other hand, has a F/H ratio of 13/4, containing much more fluorine than hydrogen. For these reasons, one might expect the Fluoropropyl POSS to be more compatible with the PVdF than the Fluorooctyl POSS. This is, indeed, what is observed. Figure 3 is a 1.0 μm AFM image of a Fluoropropyl POSS/PVdF blend. The POSS seems well dispersed with the polymer lamellae clearly visible in the phase image. Figure 4 is a 5 μm AFM image of a Fluorooctyl POSS/PVdF blend. Large POSS aggregates appear to have formed in the polymer sample.

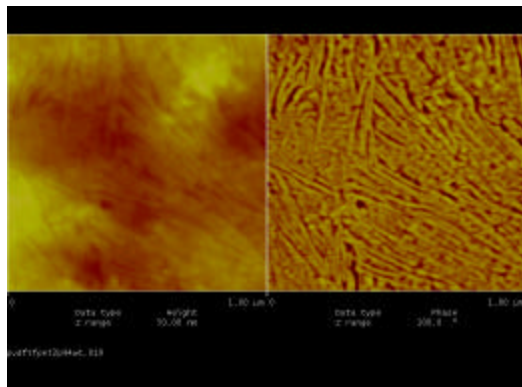


Figure 3. AFM image showing the largely compatible Fluoropropyl POSS in PVdF.

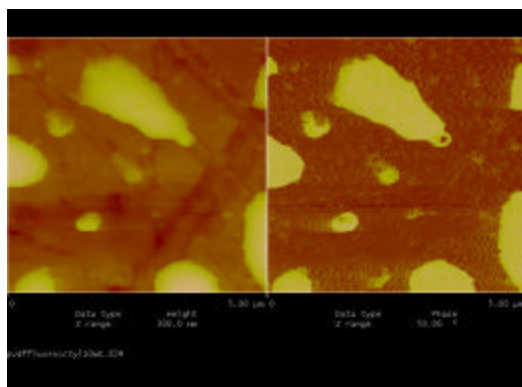


Figure 4. AFM image showing the largely incompatible Fluorooctyl POSS in PVdF.

Another tool used to determine dispersion is the element mapping capability of SEM. Cross-sectional samples of Fluoropropyl/PVdF films were examined using this capacity. The element maps are in color and, therefore, are not shown in the paper. However, the silicon map shows excellent dispersion in the PVdF matrix. Quantification of the dispersion will soon be underway.

3.2.2 Processability The processability of the samples were compared using torque and load, a measure of the pressure generated in the mixer, of the compounder motor. The pressure is generated in the mixer due to the conical design of the mixer. For a constant volume of material

compounded and a fixed screw speed, the pressure generated is proportional to the viscosity of the material. The lower the pressure, the lower the viscosity, and the easier the material is to process. The second measure of processability is the torque output by the motor. This gives an indication of the mechanical energy put into the system and is proportional to the current used by the motor. Hong et al. utilized a similar measure to characterize the processability of polyethylene and hyperbranched polymer blends (13). The lower the torque output the more processable the polymer (for a given screw speed).

These two measures of the processability of the polymer blends were recorded at 30 sec. intervals during processing. It was found, within a 95% confidence interval, that the load and torque values were constant for the duration of processing excluding the first 30 sec. Therefore, an average value for both torque and load is assigned to each processing run. In order to investigate the effect of the addition of FluoroPOSS, relative torque and relative load values were computed utilizing the average values in comparison to the average values found for the unfilled resins. Figure 5 and Figure 6 show the relative torque and load values with respect to the weight percentage of POSS added. The former illustrates the data for the FEP blends and the latter shows the results for the PCTFE blends. The solid symbols represent the relative torque values where the relative load results are illustrated by the open symbols. The square symbols symbolize the results of the fluorodecyl POSS blends and the circular symbols show the fluoro-octyl POSS blend results. One will notice that 10 weight percent of either POSS in FEP improves the processability of the polymer by greater than 40 percent and the addition of another 5 weight percent further improves the torque and load by approximately 10 and 20 percent, respectively. The effect on PCTFE is not as pronounced but the processability is still improved by greater than 30 percent. In addition, the fluorodecyl POSS exhibits a greater effect on the torque and load for the PCTFE blends.

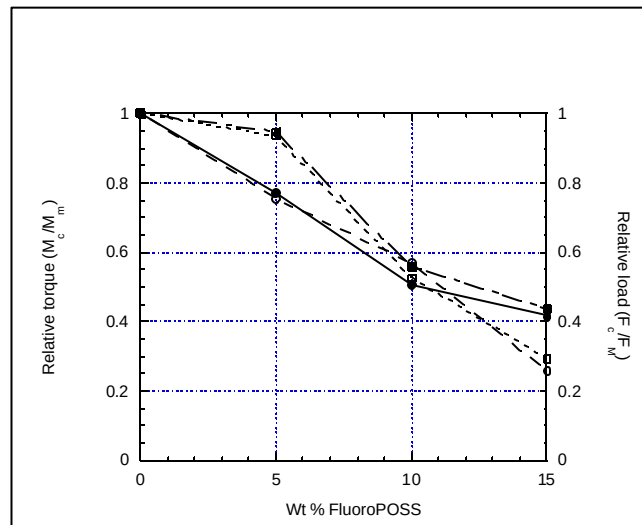


Figure 5. Effect of FluoroPOSS on processing variables torque and load for FEP blends.

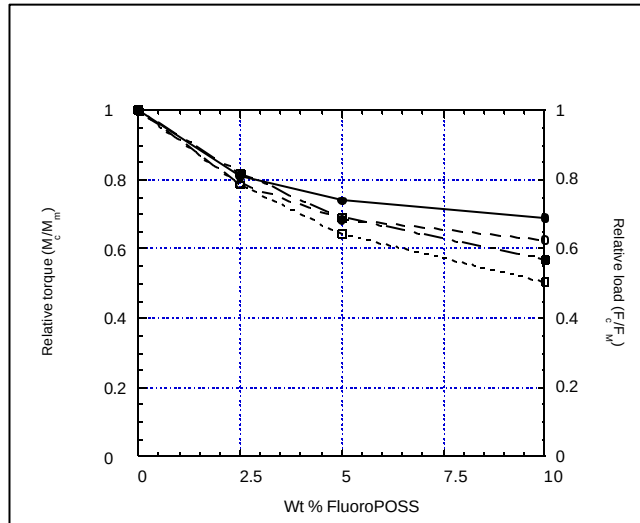


Figure 6. Effect of FluoroPOSS on processing variables torque and load for PCTFE blends.

3.2.3 Thermo-mechanical Analysis The thermal stability of the polymer blends are investigated by thermal gravimetric analysis (TGA). Initially the FluoroPOSS compounds are investigated. For this analysis, a five percent weight loss is defined as the volatilization temperature. It was found that the Fluorooctyl POSS has a volatilization temperature of approximately 280 °C and the Fluorodecyl POSS volatilizes at approximately 325 °C.

The TGA of the unfilled FEP indicates that there is a 16% weight loss at 500 °C and if 15 weight percent of either FluoroPOSS is added to FEP, there is only an additional 8% weight loss at 500 °C. This indicates that a portion of the FluoroPOSS is bound to the FEP, even in the melt state and above the volatilization temperature of the FluoroPOSS.

In order to determine the effect of the FluoroPOSS on the mechanical properties of FEP and PCTFE, dynamic mechanical analysis (DMTA) was performed. Figures 7 and 8 illustrate the storage moduli for the FEP and PCTFE blends, respectively. In Figure 7, one will notice that there may be a small decrease in modulus, which may not be statistically significant, for the 5 and 10 weight percent FEP blends with either variety of FluoroPOSS. Figure 8 shows the storage modulus data for the PCTFE blends. Again, one will notice only a small decrease in the modulus values between the filled and unfilled samples.

Figures 9 and 10 show the loss moduli for the FEP and PCTFE blends. One will notice that, similar to the storage modulus curves in Figure 7, the loss moduli of the FEP blends, shown in Figure 9, are very similar to the unfilled FEP curve with only a slight decrease. The loss moduli of the PCTFE/FluoroPOSS blends shown in Figure 10, follow the trend seen in the previous figures. We again see that the mechanical properties of the fluoropolymers are only slightly altered by the addition of FluoroPOSS. The possible exception to this is the composite with 10

weight percent Fluorodecyl POSS. This sample was very difficult to mold into quality films for testing. The poor quality of the films tested may lead to the scatter seen in the data and possibly the lower temperature for the peak in the loss modulus curve. For this study, the glass transition temperature of the polymer is defined as the peak in the loss modulus curves. The addition of FluoroPOSS to FEP and PCTFE decreases the glass transition temperature approximately two degrees. This is shown in Figures 9 and 10. The variation in glass transition temperature seen with the addition of FluoroPOSS is small enough to be statistically insignificant.

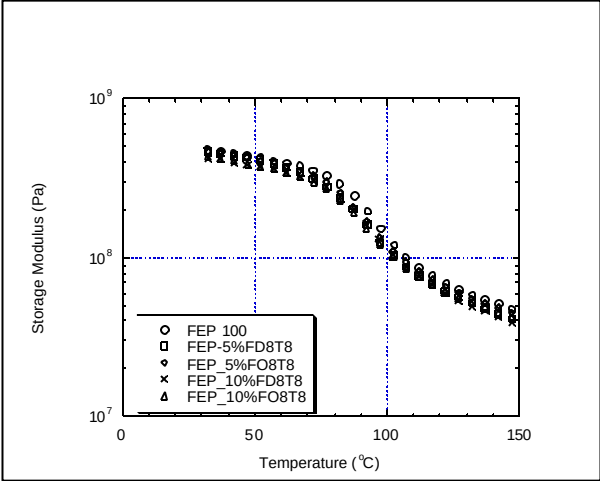


Figure 7. Storage modulus data for FluoroPOSS/FEP films.

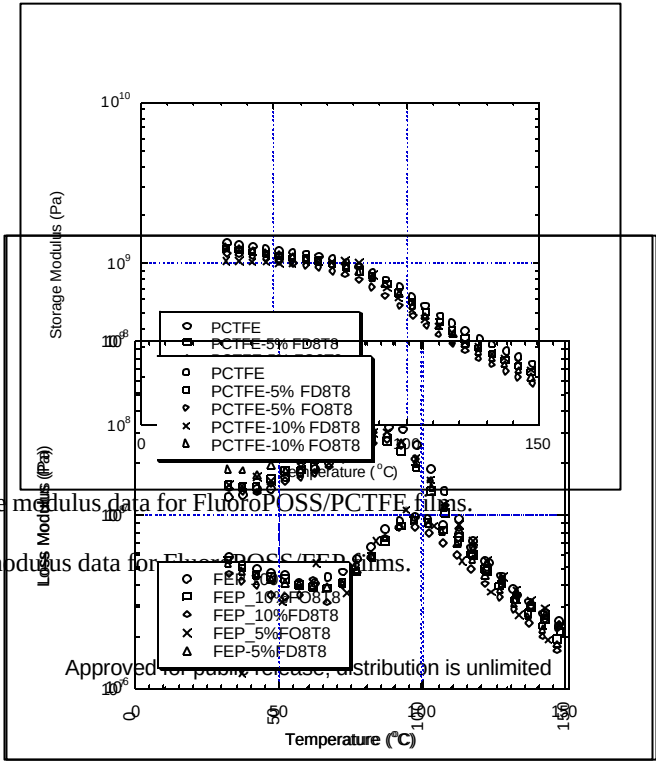


Figure 8. Storage modulus data for FluoroPOSS/PCTFE films.

Figure 9. Loss modulus data for FluoroPOSS/FEP films.

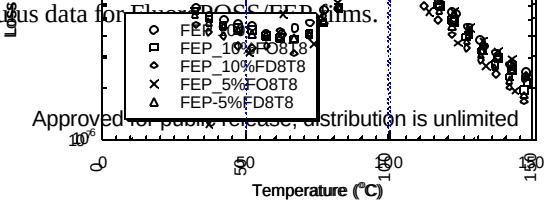


Figure 10. Loss modulus data for FluoroPOSS/PCTFE films.

3.2.4 Surface Properties While fluoropolymers are known for their hydrophobicity and low coefficients of friction, incorporation of FluoroPOSS may help to improve these properties even further. Water contact angles are a measure of surface hydrophobicity and provide insight into the free energy of the surface. Contact angles have been obtained on FEP and PCTFE nanocomposites containing Fluorooctyl and Fluorodecyl POSS.

Technologies that may benefit from the blending of FluoroPOSS into fluoropolymers include abrasion resistance, lubricity, anti-icing, and non-wetting applications. Figure 11 shows a drop of water on the surface of a PCTFE film. The contact angle was measured at 88° . Figure 12 shows a drop of water on the surface of a PCTFE blend containing 10% Fluorodecyl POSS. The contact angle for this film was measured at 128° . There is a 40° increase in contact angle with just 10% added Fluorodecyl POSS.

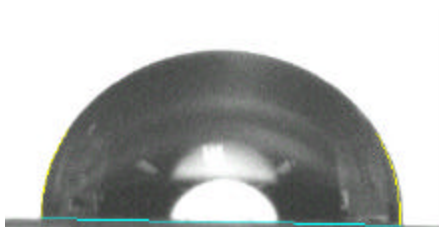


Figure 11. Water contact angle of 88° on PCTFE film.

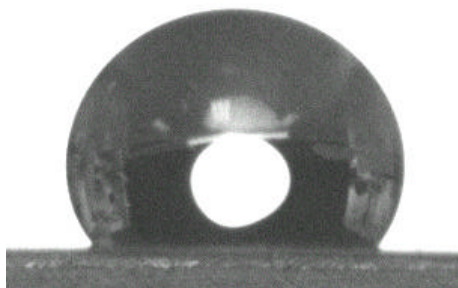


Figure 12. Water contact angle of 128° on PCTFE film containing 10% Fluorodecyl POSS.

A graph of the contact angle change in FEP nanocomposites containing Fluorooctyl and Fluorodecyl POSS is shown in Figure 13. Figure 14 is a graph showing the contact angle change in PCTFE nanocomposites containing both POSS materials. It has also been observed, as one might expect, that the contact angle increases with increasing weight percent POSS. Contact angles have been obtained on other fluoropolymers as well. All show a similar trend. It should be noted that a surface with a contact angle of 90° or higher is considered a “non-wetting”

surface, while a surface with a contact angle below 90° is considered “wetting.” Figure 14 shows that unfilled PCTFE has a contact angle of 88°. Addition of FluoroPOSS produces a “non wetting” surface.

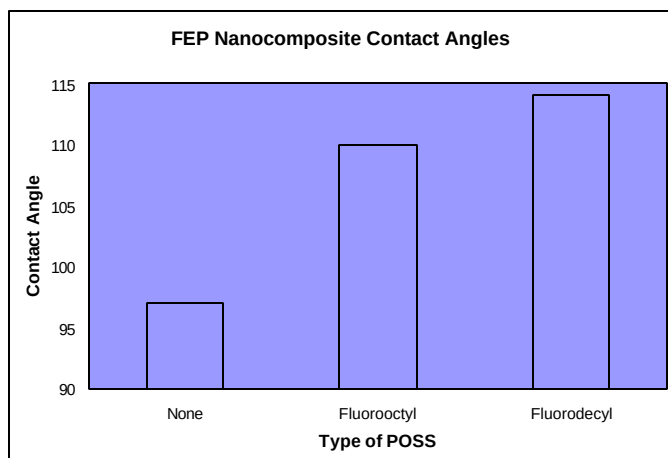


Figure 13. Contact angle measurements of FluoroPOSS/FEP nanocomposites.

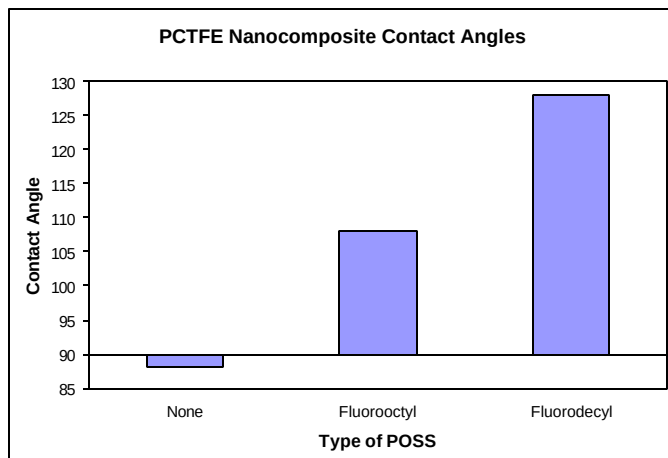


Figure 14. Contact angle measurements of FluoroPOSS/PCTFE nanocomposites.

4. CONCLUSIONS

A number of fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS) have been blended into a variety of fluoropolymers. These fluoropolymers include fluorinated ethylene-propylene (FEP), poly(chlorotrifluoroethylene) (PCTFE), and poly(vinylidene fluoride) (PVdF). The POSS blendables appear to be well dispersed in both scanning electron microscopy (SEM) and atomic force microscopy (AFM) spectra. The alkyl groups on the POSS cages help

determine with which polymer systems the POSS will be miscible. These POSS fluoropolymers may be useful as low friction surfaces or hydrophobic coatings. Contact angle measurements of the POSS fluoropolymers show an improvement of water contact angles over the unfilled materials. Fluorodecyl POSS/PCTFE shows a contact angle improvement of 40° over the unfilled material. The low surface energy POSS compounds also appear to act as a processing aid during fluoropolymer processing, significantly reducing both the torque and load measurements in the extruder. Thermal and mechanical properties of the blended fluoropolymers do not differ significantly from those of the unfilled polymers.

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6. REFERENCES

1. POSS is a registered trademark of Hybrid Plastics Inc., Fountain Valley, CA 92708
2. R. I. Gonzalez, S. H. Phillips, and G. B. Hoflund, Spacecraft and Rockets J., **37**, 463 (2000).
3. G. B. Hoflund, R. I. Gonzalez, and S. H. Phillips, Adhesion Sci. Technol. J., **15**, 1199 (2001).
4. J. W. Gilman, D. S. Schlitzer, and J. D. Lichtenhan, Appl. Polym. Sci. J., **60**, 591 (1996).
5. S.-Y. Lu, I. Hamerton, Prog. Polym. Sci., **27**, 1661 (2002).
6. G. Z. Lee, L. Wang, H. Toghiani, T. L. Daulton, and C. U. Pittman Jr., Polymer, **43**, 4167 (2002).
7. W. Zhang, B. X. Fu, E. Schrag, B. Hsiao, P. T. Mather, N.-L. Yang, D. Xu, H. Ade, M. Rafailovich, and J. Sokolov, Macromolecules, **35**, 8029 (2002).
8. B.X. Fu, M. Y. Gelfer, B. S. Hsiao, S. Phillips, B. Viers, R. Blanski, P. Ruth, Polymer, **44**, (5), 1499 (2003).
9. J. Deng, J. T. Polidan, J. R. Hottle, C. E. Farmer-Creely, B. D. Viers, and A. Esker, Am. Chem. Soc. J., **124**, (51), 15194 (2002).
10. B. X. Fu, B. S. Hsiao, H. White, M. Rafailovich, P. T. Mather, H. G. Jeon, S. Phillips, J. Lichtenhan, J. Schwab, Polymer Int., **49**, (5), 437 (2000).
11. J. M. Mabry, A. Vij, B. D. Viers, R. L. Blanski, C. E. Schlaefer, Angew. Chem. Int. Ed. Engl., Manuscript in preparation.
12. K. Dedecker and G. Groeninckx, Polymer, **39**, 4993 (1998).
13. Y. Hong, J. J. Cooper-White, M. E. Mackay, C. J. Hawker, E. Malmstrom, and N. Rehnberg, Rheol. J., **43**, 781 (1999).