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14. ABSTRACT Polyhedral oligomeric silsesquioxanes (POSS) are nanoparticles that are used to enhance the thermal and mechanical properties of polymeric systems and are being examined for use in many applications. These applications include space-survivable coatings and fire-resistant materials. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, thus affecting both thermal and mechanical properties. Polymeric materials are typically tough, lightweight, and easy to process. However, they often lack resistance to oxidation and degrade at high temperatures. Ceramic materials, on the other hand, are thermally stable and have high oxidative resistance, but are brittle and difficult to process. POSS materials contain a thermally robust inorganic core that is surrounded by an organic corona (figure 1), which increases miscibility with a polymer. Because of a wide range of available organic functionalities, POSS have been incorporated into many polymer systems and found to improve the polymer thermo-oxidative stability.					
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POLYMER NANOCOMPOSITES DESIGNED WITH POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS) AND PLASTICS

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are nanoparticles that are used to enhance the thermal and mechanical properties of polymeric systems and are being examined for use in many applications.¹⁻² These applications include space-survivable coatings³⁻⁵ and fire-resistant materials.⁶⁻⁸ Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, thus affecting both thermal and mechanical properties.

Polymeric materials are typically tough, lightweight, and easy to process. However, they often lack resistance to oxidation and degrade at high temperatures. Ceramic materials, on the other hand, are thermally stable and have high oxidative resistance, but are brittle and difficult to process. POSS materials contain a thermally robust inorganic core that is surrounded by an organic corona (figure 1), which increases miscibility with a polymer. Because of a wide range of available organic functionalities, POSS have been incorporated into many polymer systems and found to improve the polymer thermo-oxidative stability.

RSiX₃ acid or base hydrolysis → RSiO_{1.5}

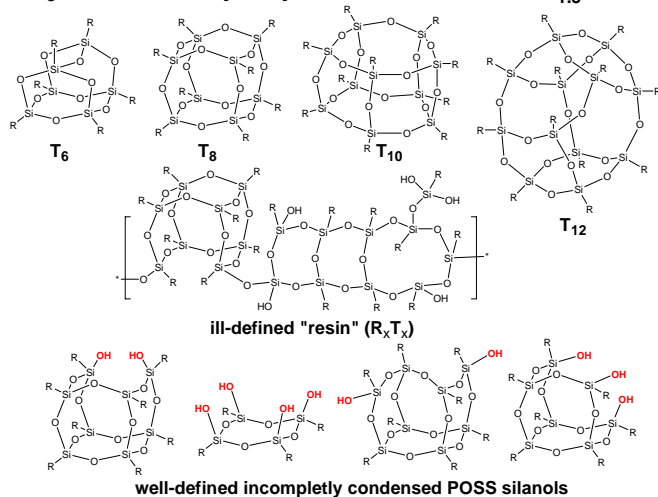


Figure 1. Acid- or base-catalyzed hydrolysis of trifunctional silanes will produce POSS materials with an inorganic framework and a corona of organic R groups to compatibilize the silica core with an organic plastic.

POSS are typically produced by the acid- or base-catalyzed hydrolysis of trifunctional silanes (figure 1).⁹ POSS compounds can be produced as either completely or incompletely condensed cage structures. The completely condensed compounds commonly contain cages with six to twelve silicon atoms, although T₈ and T₁₂ cages can be prepared selectively. Incompletely condensed cages typically contain four to eight silicon atoms and still retain reactive silanol groups. The yields for these reactions are often nearly quantitative, depending on the R-groups. The typical reaction byproduct is an ill-defined resinous material that is formed when the condensation is less controlled. This resin may contain partial cage structures and ladder structures, etc. Fortunately, the resin is typically soluble, allowing its removal by extraction in various solvents.

Results and Discussion

POSS compounds are typically used to improve the mechanical properties of polymers. This is often done by the blending of completely condensed POSS cages into polymers in which they are miscible. Thermal properties of the POSS compounds are quite important because many

polymers have high melt-processing temperatures. The POSS compound to be blended into the polymer must not only be highly miscible in the polymer but must be thermally stable beyond the polymer processing temperature. Fortunately, POSS compounds volatilize or degrade at temperatures up to 400 °C. This high temperature stability allows the blending of many of these POSS compounds to improve properties of various polymer systems. In addition to melt-blending, POSS can be chemically bound to the polymer backbone (figure 2). This is usually done one of two ways. The first method involves the direct copolymerization of POSS monomers during polymerization. This has been done in both step-growth and chain-growth polymerizations. The second method for binding POSS to the polymer backbone involves the chemical modification of preformed polymers and results in the POSS being pendant to the polymer backbone. It has been observed that pendant POSS produce superior thermal and mechanical properties in the polymers to which they are attached when compared to similar polymers just blended with POSS.

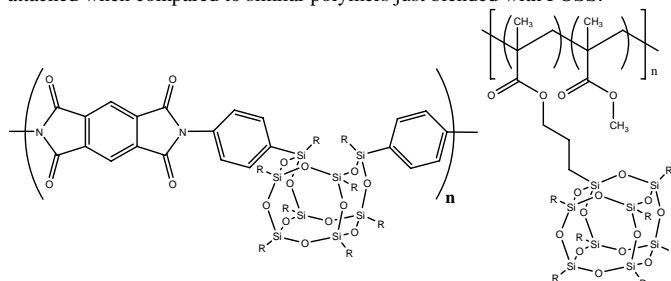


Figure 2. Two polymer architectures with POSS formed by (a) step-growth polymerization and (b) grafting or chain-growth polymerization

Many varieties of POSS compounds are now commercially available; hydrophobic, hydrophilic and fluorophilic derivatives enable a vast number of potential applications. The use of these and other POSS compounds in various polymer systems will be discussed.

Conclusions

Polyhedral oligomeric silsesquioxanes (POSS) contain inorganic cores with organic coronae to provide polymer miscibility. They may also possess reactive groups for polymer grafting or copolymerization. These compounds have been produced by the acid- or base-catalyzed hydrolysis of trifunctional monomers to produce both completely and incompletely condensed cage structures. POSS have been incorporated into both organic and inorganic polymers and shown to improve both thermal and mechanical properties.

Acknowledgments

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