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Timothy S. Haddad (ERC); Andre Lee; Shawn H. Phillips, "Polydimethylsiloxanes Modified with Inorganic Polyhedra" (Paper)  
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POLY(DIMETHYLSILOXANES) MODIFIED WITH INORGANIC POLYHEDRA

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Introduction

There has been recent interest in using polyhedral oligomeric silsesquioxanes (POSS) as molecular building blocks in many polymer systems. This interest is driven by significant property enhancements imparted by dispersion of a covalently bound nanosized inorganic particulate into an organic matrix. Most of the work to date has focused on thermoplastic hybrid inorganic/organic polymers derived from either a triol- or a diol-silsesquioxane (Figure 1).

Figure 1. Two types of incompletely condensed silsesquioxanes used for making hybrid inorganic/organic materials.

Diisilanol 1 can be directly condensed with chloro-terminated oligodimethylsiloxane fragments to make alternating “bead” siloxane copolymers (Figure 2). The most significant effect of placing a large POSS cage directly into the main polymer chain is a huge increase in glass transition from −125 °C for normal polydimethylsiloxane (PDMS) to about −65 °C.

Figure 2. Diisilanol 1 converted into an alternating AB siloxane copolymer.

Trisilanol 2 can be converted into a fully condensed POSS cage containing a single allyl group. The allyl group can be hydrosilylated to short chain poly(dimethyl-co-methylhydrido)siloxane fragments to make “pendant” type siloxane copolymers (Figure 3). Large increases in the Tg are again observed, but the effect is slightly less than that seen in the “bead” copolymers.

Figure 3. Trisilanol 2 can be derivatized and then appended to short chain poly(dimethyl-co-methylhydrido)siloxanes.

Both “bead” and “pendant” type siloxanes are low degree of polymerization polymers, such that it was not possible to reveal what effect a small weight % of POSS would have on polymer properties. Because a single POSS cage weighs approximately 1000 grams/mole, even a lone POSS cage on a short PDMS chain can take up a significant portion of the weight and/or volume % of the copolymer. To accommodate this disparity in molecular weight between a POSS moiety and a PDMS repeat unit, we decided to graft a POSS-hydride onto high molecular weight poly(dimethyl-co-methylhydro)siloxanes, followed by 1.2 mL of a xylene solution (1.9 % Pt) of Karstedt’s catalyst and the solution stirred under nitrogen overnight. The next day, 18 mg of Me3SiOSiMe2H was added to react with any remaining vinyl functionality. After stirring overnight the POSS-grafted copolymer was isolated by precipitation into methanol and then dried in a vacuum oven overnight at 50 °C. The yield of product is virtually quantitative. The exact same procedure was followed for producing POSS-PDMS blends except that the platinum catalyst was left out.

Results and Discussion

Synthesis of graftable POSS-hydrides. The readily available POSS-trisilanol 3a,b,c are easily converted into monohydrides useful in hydrosilation based grafting reactions. The trisilanol react with siliconchloroalchloride in the presence of NEt threefold condensed POSS with a single Si–Cl functionality. This bond can be hydrosilylated with water to make a POSS-monohydride, which in turn can be reacted with Me3SiOH to form the POSS-hydrides, 3a,b,c (See Figure 4).

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Hydroisilations of poly(dimethyl-co-methylvinyl)siloxane with a POSS-hydrde. Two high molecular weight vinyl-containing PDMS polymers were chosen for grafting with the POSS-hydrdes. One derivative has a degree of polymerization of about 1710 and contains, on average, 7.6 vinyl groups per chain, the other has a degree of polymerization of about 1840 and contains about 66 vinyls per average polymer chain. Completely grafting all of the vinyls on first polymer gives a polymer with only about 2.5 weight % POSS and no observable change. Control reactions proved that the observed effects were due to the POSS and not from any post-isolation "curing" of the PDMS being investigated.

Conclusions

The synthesis and effect of covalently tethering a POSS cage to a high molecular weight PDMS backbone over a range of low POSS weight percentages was investigated and compared to just blending equivalent amounts POSS into PDMS. Significant effects were noted even at POSS loadings as low as 2.5 weight %. Grafting about 5 weight % of CpsSiO2(OSiMe2H) onto the PDMS slows the characteristic relaxation time of the polymer by about one order of magnitude. By comparison, blending 5 weight % of POSS with the same PDMS effects no observable change.

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References


