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Communications

Synthesis and Properties of New Poly(Dimethylsiloxane) Nanocomposites

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Introduction

The field of polymer nanocomposites has recently attracted considerable attention, as researchers strive to enhance polymer properties and extend their utility by using molecular or nanoscale reinforcements instead of the more conventional particulate-filled, microcomposites.^{1,2} We and others have specifically focused on polymer nanocomposites using layered mica-type silicates (MTSs).³⁻¹⁹ Two types of nanocomposites representing the end members of a structural hierarchy

are possible: (a) **intercalated**, in which extended polymer chains are intercalated between the host layers resulting in a well-ordered multilayer, and (b) **delaminated**, in which the host layers (1 nm thick) are dispersed in a continuous polymer matrix. In contrast to the intercalated hybrids, the interlayer expansion in delaminated hybrids is comparable to the radius of gyration of the polymer, and the host layers have lost their structural registry.

Delaminated nanocomposites attain a particular degree of stiffness, strength, and barrier properties with far less ceramic content than in conventionally filled polymers. They are, therefore, far lighter in weight, and they also exhibit dimensional stability in two dimensions (rather than in one). Workers at the Toyota Research Center have demonstrated, for example, that MTS-nylon nanocomposites exhibit substantial improvements in strength and modulus compared to the unfilled polymer without sacrificing impact resistance.¹⁰⁻¹⁵ More importantly the nanocomposites show a substantial increase in the heat distortion temperature extending the use of nylon to under-the-hood structural parts in the engine compartment. Similarly epoxy nanocomposites display significant increases in modulus and tensile strength.¹⁶⁻¹⁸ The increase in modulus is much more pronounced when the matrix is in the rubbery state. In addition, MTS-nanocomposites exhibit dramatically improved barrier properties.¹⁹

Since nanocomposites achieve composite properties at a much lower volume fraction of reinforcement, they avoid many of the costly and cumbersome fabrication techniques common to conventional fiber- or mineral-reinforced polymers. Instead nanocomposites can be

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processed by techniques such as extrusion, injection molding, and casting normally used with unfilled polymers. Also, in addition to offering simplified manufacturing, nanocomposites are adaptable to films, fibers, and monoliths.

Synthesis of nanocomposites has typically involved intercalation of a suitable monomer followed by polymerization. An integral role of the monomer is to promote delamination and dispersion of the host particles. Various monomers have been used, yielding linear and cross-linked polymer matrixes.

For most technologically important polymers the monomer intercalation/delamination approach is rather limited because a suitable monomer is not always available. We have recently discovered a more versatile and environmentally benign approach based on direct polymer melt intercalation. The process involves heating a polymer-silicate mixture either statically or under shear in an extruder above the softening temperature of the polymer. Polymers have included polystyrene,²⁰ poly(ethylene oxide),²¹ cellulose, polyamides, liquid-crystalline polyesters, polyphosphazenes, and others.²² Depending on the polymer, pristine or alkylammonium-exchanged silicates (to render their surface hydrophobic) can be used.

Elastomeric-MTS nanocomposites remain a relatively unexplored field. Siloxanes have been traditionally reinforced with silica.²³ Agglomeration of the silica particles, however, often prevents full realization of the filler capability. One way to aid dispersion is by functionalizing the silica particles with silanes.²⁴ Recently, novel inorganic/organic hybrids have been synthesized using sol-gel techniques by precipitating silica particles during polymer network formation or in precursor-swollen polymer matrices.²⁵ Alternatively, siloxanes have been functionalized with alkoxy groups, allowing active polymer participation in the silica-formation process.²⁶ In addition, the reinforcing properties of porous zeolites have been explored.²⁷

We report here the first melt-processed MTS-poly(dimethylsiloxane) nanocomposites. The synthesis involves delamination of the silicate particles in the PDMS matrix followed by cross-linking. The resulting nanocomposites exhibit significantly improved thermal and swelling properties compared to the unfilled or more conventionally filled siloxanes.

Experimental Section

The nanocomposites were synthesized by sonicating at room temperature for 2 min a silanol-terminated poly(dimethylsiloxane) (PDMS, $M_w = 18\,000$, United Chemical Technologies, Inc.) and a commercial organosilicate (SO 4682, Southern Clay Products). The organosilicate is prepared by ion exchanging Na^+ -montmorillonite with a cation exchange capacity of 90

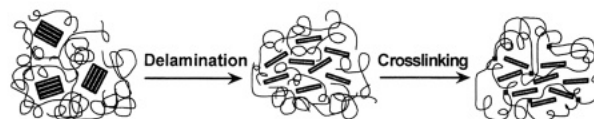


Figure 1. Schematic illustration of nanocomposite synthesis.

mequiv/100 g with dimethyl ditallow ammonium bromide which contains 70, 25, 4, and 1% of C_{18} , C_{16} , C_{14} , and C_{12} , respectively. Cross-linking was accomplished by adding to the mixture tetraethyl orthosilicate (TEOS, Aldrich Chemical) and tin 2-ethylhexanoate (Chemat) and sonicating an additional 2 min. The samples were then cast into Teflon molds and cured at room temperature under vacuum for a minimum of 12 h.

X-ray diffraction analysis was performed using a Scintag θ - θ diffractometer and $\text{Cu K}\alpha$ radiation. Swelling data were obtained using a standard mass differential technique.²⁸ Samples of a known weight were immersed in toluene at room temperature and reweighed periodically after blotting to remove excess solvent. The difference between two weighings corresponded to toluene uptake. Samples were weighed until reaching constant weight, at which point it was assumed that they had reached equilibrium. Thermal analysis was performed on a DuPont Instruments 9900 thermal analyzer at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under flowing nitrogen.

Results and Discussion

A schematic of nanocomposite synthesis is illustrated in Figure 1. Delamination of the silicate particles in the PDMS matrix is accomplished by suspending the organosilicate in PDMS at room temperature and sonicating. An important measure of the degree of silicate dispersion and delamination is usually obtained by X-ray diffraction measurements. Generally intense reflections in the range $2\theta = 3\text{--}9^\circ$ indicate an ordered intercalated system with alternating polymer-silicate layers. In delaminated hybrids, on the other hand, where single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix, XRD patterns with no distinct features in the low 2θ range are anticipated due to the loss of structural registry.

Shown in Figure 2 is a series of XRD patterns of PDMS nanocomposites containing various silicate loadings. The featureless patterns suggest that delaminated hybrids are present. For comparison the pattern of a PDMS hybrid containing 5 wt % of a bentonite exchanged with benzyldimethyloctadecylammonium salt (BDMO) and processed in an identical fashion with the other hybrids is also included. The latter pattern exhibits a distinct reflection with a d spacing identical with that of the organosilicate used suggesting that neither intercalation of the polymer chains nor delamination has taken place. Furthermore, XRD analysis of hybrids prepared from a PDMS-poly(diphenylsiloxane) random copolymer containing 14-18 mol % diphenylsiloxane suggests that an intercalated rather than a delaminated hybrid is formed. Both observations underlie the importance of matching the matrix-organosilicate interactions in order to optimize silicate delamination/dispersion.

Silicate delamination was optimized by adding water during the initial sonication. Figure 3 is a series of XRD patterns of PDMS nanocomposites prepared using different amounts of water. The optimum water concentration for which no discernible reflection is observed

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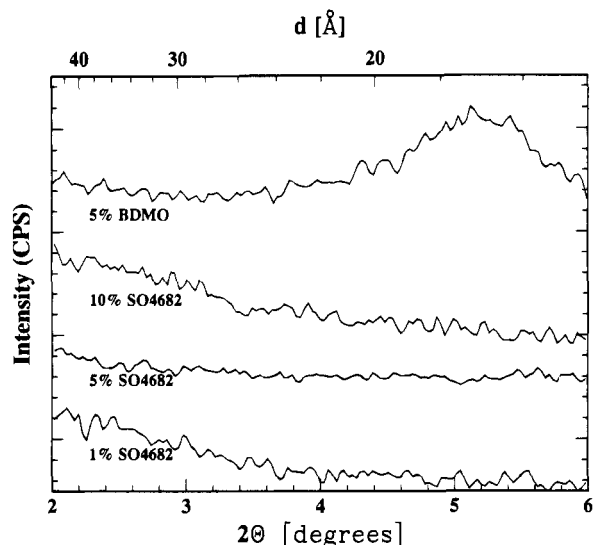


Figure 2. X-ray diffraction patterns of PDMS nanocomposites containing various amounts of organosilicate. The top pattern corresponds to a hybrid prepared using 5 wt % of BDMO instead of the SO 4682 used in the other hybrids.

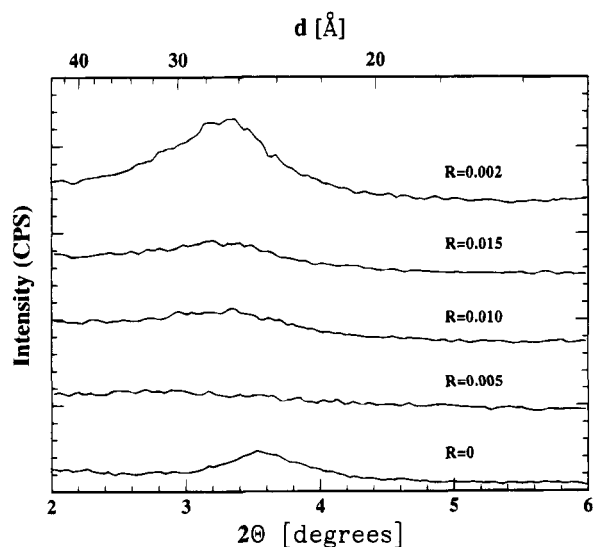


Figure 3. X-ray diffraction patterns of nanocomposites as a function of water content. R is the weight ratio of water to silicate.

corresponds to about a monolayer coverage on the silicate surface. (For $R > 0.010$ the XRD traces show a reflection with an increased d spacing due to intercalation of water molecules but no delamination; interestingly the surface characteristics are no longer conducive of delamination in the PDMS matrix.)

The superior mechanical properties of siloxanes at elevated temperatures usually justify their increased cost over conventional elastomers.²⁹ Thus, thermal stability especially at elevated temperatures is an important characteristic in these materials. Figure 4 show the TGA analysis for both the unfilled PDMS and the PDMS nanocomposite containing 10 wt % SO4682. The nanocomposite shows delayed decomposition compared to the unfilled polymer. PDMS is well-known to decompose into volatile cyclic silicates.³⁰ Since the

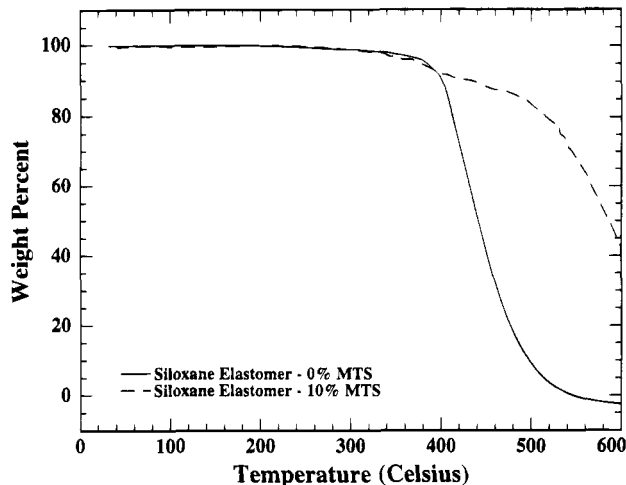


Figure 4. TGA traces for PDMS (solid line) and PDMS nanocomposite (dashed line) containing 10 wt % silicate.

permeability of the nanocomposites is dramatically decreased,¹³ we attribute the increased thermal stability to hindered outdiffusion of the volatile decomposition products.

Additionally, the nanocomposites exhibit a substantial decrease in solvent uptake compared to the unfilled PDMS matrix (Figure 5). The nanocomposites show a significant decrease in swelling even for filler loadings as low as 1 vol %, as indicated by the reduced solvent uptake expressed as V_{ro}/V_{rf} . The subscripts o and f refer to the unfilled and filled nanocomposites, respectively, with

$$V_r = \frac{\text{volume of unswollen polymer matrix}}{\text{volume of swollen polymer matrix}}$$

Kraus has previously shown that plots of V_{ro}/V_{rf} versus filler content, ϕ , corrected for the nonswelling filler, are indicative of filler reinforcement ability.³¹ Strongly interacting fillers reduce swelling, while non-reinforcing fillers result in solvent uptake which may exceed that of the unfilled polymer. This behavior has been previously attributed to the formation of "bound polymer", polymer in close proximity to the filler which is either physisorbed or chemisorbed and therefore restricts swelling. Nonreinforcing fillers prevent the formation of bound polymer, allowing large vacuoles to form during solvent exposure, resulting in increased solvent uptake. The strong swelling suppression in the nanocomposites indicates a rather strong filler reinforcement. This is in contrast to more conventionally filled elastomers such as styrene butadiene rubber (SBR) filled with kaolin, also a layered silicate, which exhibits increased swelling (inset in Figure 5).³²

Kraus has also shown that solvent uptake is inversely proportional to the filler reinforcing strength which strongly depends on filler surface area and agglomerate structure. As shown in the inset of Figure 5, the nanocomposites swell less than carbon black filled elastomers. This behavior can be explained in part by the large surface area of layered silicates ($750 \text{ m}^2/\text{g}$)³³ compared to 13–100 m^2/g for unaggregated carbon

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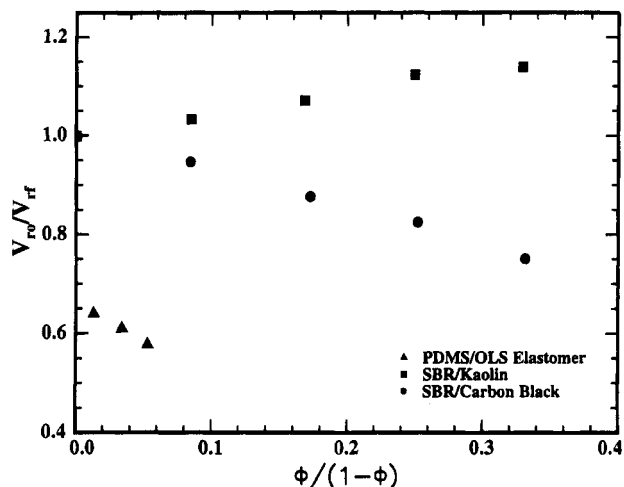


Figure 5. Relative toluene uptake for PDMS nanocomposites versus filler concentration corrected for the nonswelling filler.

black. Thus, the dramatic decrease in solvent uptake is due to the strong interactions between polymer and silicate and the nanodispersion which maximizes the available surface area of the reinforcing phase. Recently, PDMS filled with in situ precipitated silica and titania particles has been found to behave in a similar manner.³⁴ Further analysis of the swelling data is underway and will be presented in a future publication.

In summary, PDMS-silicate nanocomposites have been synthesized by melt processing. The synthesis involves silicate delamination in the polymer matrix followed by cross-linking. Delamination is accomplished by fine-tuning organosilicate-polymer interactions (i.e., properly matching the organosilicate with the polymer matrix). In addition, delamination is optimized by water additions corresponding to about a monolayer coverage on the surface. The nanocomposites exhibit decreased solvent uptake and increased thermal stability, attributes which make them very attractive for future applications. The increased swelling resistance is attributed to strong reinforcement/matrix interactions and the large surface area attainable by delamination and dispersion of the silicate particles in the polymer matrix.

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