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TITLE: Polymer-Layered Silicate Nanocomposites: Emerging Scientific
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TITLE: NATO Advanced Research Workshop on Nanostructured Films
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POLYMER-LAYERED SILICATE NANOCOMPOSITES: EMERGING SCIENTIFIC AND COMMERCIAL OPPORTUNITIES

Emmanuel P. Giannelis

*Department of Materials Science and Engineering
Cornell University, Ithaca, NY 14853, USA*

ABSTRACT: Polymer nanocomposites represent a radical alternative to conventionally (macroscopically) filled polymers. Because of their nanometer-size dispersion the nanocomposites exhibit markedly improved properties when compared to the pure polymers or conventional composites. These include increased modulus and strength, outstanding barrier properties, increased solvent and heat resistance and decreased flammability. In this paper the physical and mechanical properties of nanocomposites are reviewed and discussed in terms of their static and dynamic properties.

1. Introduction

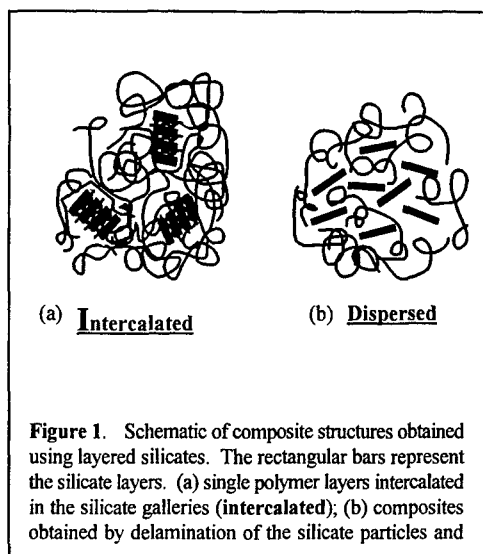
Polymer nanocomposites represent a radical alternative to conventionally filled polymers. Because of their nanometer-size dispersion the nanocomposites exhibit markedly improved properties when compared to the pure polymers or conventional composites [1]. These include increased modulus and strength, decreased gas permeability, increased solvent and heat resistance and decreased flammability [2-11]. For example, a doubling of the tensile modulus and strength without sacrificing impact resistance is achieved for nylon-layered silicate nanocomposites containing as little as 2 vol.% inorganics. In addition, the heat distortion temperature of the nanocomposites increases by up to 100 °C extending the use of the composite to higher temperature environments, such as automotive under-the-hood parts. Furthermore, the heat release rate in the nanocomposites is reduced by up to 63 % at heat fluxes of 50 kW/m² without an increase in the CO and soot produced during combustion. Applications include low-cost alternatives of high performance composites, food packaging, microelectronics and biotechnology.

2. Synthesis of Nanocomposites

Melt intercalation of high polymers is a powerful new approach to synthesize polymer-layered silicate nanocomposites [12]. This method is quite general and is broadly applicable to a range of commodity polymers from essentially non-polar polystyrene, to weakly polar poly(ethylene terephthalate) to strongly polar nylon. The nanocomposites are, thus, processable using current technologies and easily scaled to manufacturing quantities.

In general, two types of hybrids are possible: **intercalated**, in which a single, extended polymer chain is intercalated between the silicate layers resulting in well ordered polymer/inorganic multilayers, and **dispersed or disordered**, in which the silicate layers (1 nm thick) are exfoliated and dispersed in a continuous polymer matrix (Fig 1).

The silicates used belong to the general family of so-called 2:1 layered silicates. Their crystal structure consists of layers made up of two silica tetrahedra fused to an edge-shared octahedral sheet of either alumina or magnesia. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cations residing in the interlayer.



Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. Ion exchange reactions with cationic surfactants including primary, tertiary and quaternary ammonium ions render the normally hydrophilic silicate surface organophilic, which makes intercalation of many engineering polymers possible. The role of the alkyl ammonium cations in the organosilicates is to lower the surface energy of the inorganic and improve the wetting characteristics with the polymer. Additionally, the alkyl ammonium cations can provide functional groups that can react with the polymer or initiate a polymerization of monomers to improve the strength of the interface between the inorganic and the polymer.

Similarly to polymer blends any mixture of polymer and layered silicate does not necessarily lead to a nanocomposite [13]. In most cases the incompatibility of the hydrophobic polymer and the hydrophilic silicate leads to phase separation resulting in macroscopically filled systems. In contrast, by using surface modified silicates as noted earlier one can fine tune their surface energy and render them miscible (or compatible) with different polymers. The approach is based on a chemical (rather than a mechanical) driving force, which leads to nanoscopic dispersion.

3. Structure and Dynamics of Polymer Nanocomposites

The combination of enhanced modulus, strength and toughness is a unique feature of the nanocomposites. In conventionally-filled polymer systems increases in modulus typically compromise toughness. Additionally, the decrease in barrier properties of the

nanocomposites cannot be explained only on the high aspect ratio afforded by the exfoliation of the inorganic nanolayers. Alternatively we suggest that the polymer chains at the interface adopt a different structure and exhibit very different dynamics compared to the chains in the bulk. Due to the nanodispersion a very large fraction of the polymer is at the interface (close to 60%) even for a few percent inorganic. As a result these nanoscopically "confined" polymer chains contribute significantly and to a large extent control the properties of the hybrid.

Even simple notions regarding the conformations of polymers confined in two dimensions are not yet fully understood. In three dimensions, it is well known that the individual molecules in long chain polymers overlap significantly. In two dimensions, it has been suggested that the different chains overlap only slightly. Therefore, the local and global conformations of polymers in the nanocomposites are expected to be dramatically different from those observed in the bulk, not only due to the confinement of the polymer chains but also due to specific polymer-inorganic surface interactions not normally present in the bulk.

From our current theoretical and experimental studies on nanocomposites a new and quite unexpected picture is emerging [14]. Despite the presence of the "confining" inorganic layers, intercalated polymer chains exhibit substantial segmental motion even at temperatures where the polymer is normally in the glassy state. Thus, in contrast to the bulk polymers where chain mobility slows precipitously around T_g , in the nanocomposites chain mobility persists well below the bulk T_g . This behavior is counterintuitive as "confinement" of the polymer chains within ~ 2 nm is expected to increase their solid-like character and decrease their mobility.

We start with non-equilibrium dynamics present during polymer intercalation from the melt. The observation that polymer chains can undergo center of mass transport in essentially two dimensions is rather surprising because the unperturbed radius of gyration of the polymer is roughly an order of magnitude greater than the interlayer distance between the silicate layers. The ability of the polymer chains to undergo center of mass transport during intercalation is further evidence that the silicate layers do not completely restrict segmental motions, otherwise large-scale chain motion would not be possible.

Using X-ray diffraction (which monitors the angular shift and integrated intensity of the silicate reflections) we have studied the intercalation kinetics of polystyrene into organically modified silicates (Fig. 2) [15]. The effective diffusion coefficient, D_{eff} , is much faster than the tracer diffusion coefficient of the bulk polymer or the diffusion coefficient of the polymer in a thin film. This is because during intercalation polymer chains are moving down a concentration gradient, whereas in the other two cases polymer motion is entropic in origin. Furthermore, the diffusion coefficient exhibits an inverse dependence on molecular weight. Although the diffusion coefficient of polymers near surfaces has been predicted to have an inverse molecular weight dependence (and not scaled as $1/N^2$, N is the chain length, characteristic of reptation) this represents the first experimental measurement of the diffusion of high molecular weight polymer melts in two dimensions.

As the length of the surfactant molecules increases from twelve to eighteen carbon atoms, C12 to C18, respectively, the effective diffusion coefficient increases. This is because increasing the length of the surfactant chains effectively reduces the interaction with the silicate surfaces and thus decreases the stickiness to the surface.

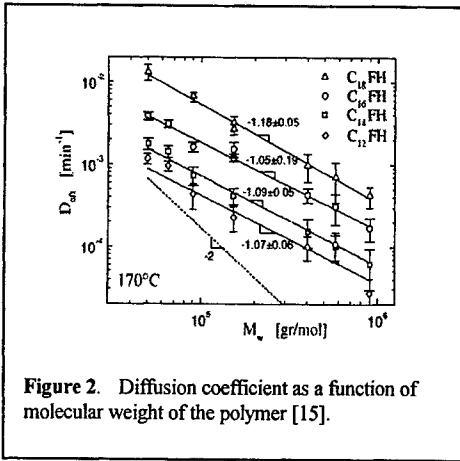


Figure 2. Diffusion coefficient as a function of molecular weight of the polymer [15].

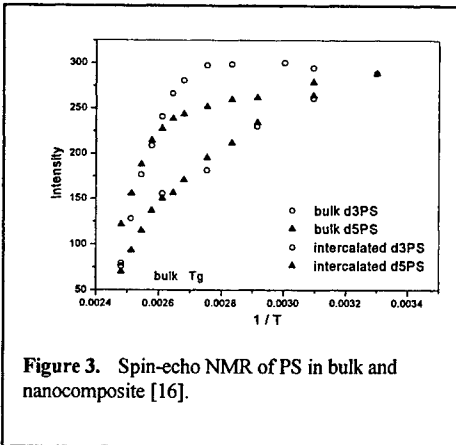


Figure 3. Spin-echo NMR of PS in bulk and nanocomposite [16].

We now turn our attention to equilibrium dynamics for the polymer chains after they have been intercalated. Local dynamics of chains “confined” between the silicate layers were probed by spin-echo NMR. In a spin-echo experiment complete refocusing of the signal is expected as long as there is no change in resonance frequency before and after the second pulse. Large intensity losses therefore take place when large amplitude dynamics commence as for example those associated with the liquid state (i.e. above the glass transition temperature, T_g).

Figure 3 shows the results of the spin-echo experiment for polystyrene and polystyrene nanocomposites [16]. To follow the respective dynamics, polystyrene deuterated at the backbone, d3, and the ring, d5, was used. When d3 polystyrene is used, the intensity of the NMR signal (multiplied by temperature) remains constant in the glassy regime followed by a large decrease above T_g . This is expected as backbone dynamics are absent below T_g and commence at T_g . There is some mobility for the d5 polystyrene below T_g , since the rings can independently flip 180° but a substantial drop in intensity is found only above the T_g . In contrast, the nanocomposites show significant amount of mobility at least for part of the polymer even at temperatures well below the T_g . Additionally, there is no distinct change from solid-like to liquid-like behavior as in the bulk polymer.

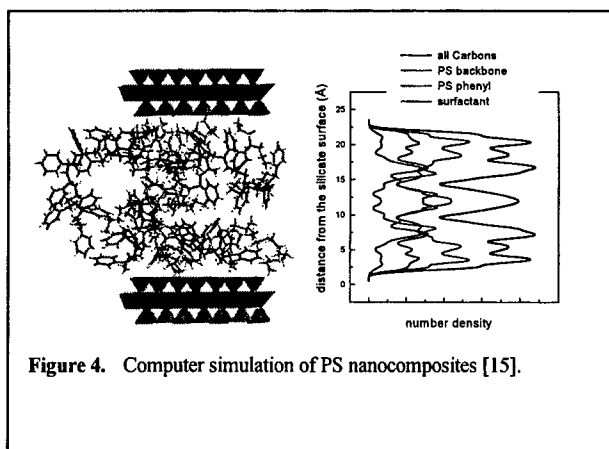


Figure 4. Computer simulation of PS nanocomposites [15].

Computer simulations offer an explanation for this behavior [15,16]. When confined between the inorganic surfaces the polymer chains order into discrete subnanometer layers (Fig. 4). This layering, clearly seen in the density profiles, imparts strong density inhomogeneity in the direction normal to the surface. The fast dynamics arise from areas of low-density or high free volume, which compensates for the confinement between the inorganic layers. Neutron scattering measurements support the above structure. The polymer chains adopt a 2D random-walk structure. Additionally, in contrast to the bulk polymer the intercalated chains do not show a single characteristic length.

4. Conclusions

Mass transport of polymer chains into the silicate layers is faster than the corresponding self-diffusion. Thus hybrid formation requires no additional processing time than currently required for conventional polymer processing techniques such as extrusion.

Despite the presence of the “confining” inorganic layers, intercalated polymer chains exhibit substantial segmental motion even at temperatures where the polymer is normally in the glassy state. Thus, in contrast to the bulk polymers where chain mobility slows precipitously around T_g , in the nanocomposites chain mobility persists well below the bulk T_g . This behavior is rationalized in terms of the new structure the polymer chains adopt at the interface. When confined between the inorganic surfaces the polymer chains order into discrete subnanometer layers. The fast dynamics arise from areas of low-density or high free volume, which compensates for the confinement between the inorganic layers. Neutron scattering measurements support the above structure.

Acknowledgements

This work was supported in part by the Cornell Center for Materials Research, AFOSR and ONR. I would like to thank my coworkers and collaborators S.D. Burnside, H. Chen, J.D.

Gilman, J. Genzer, T. Kashiwagi, E. Manias, P.B. Messersmith, E.J. Kramer, R. Krishnamoorti, R.A. Vaia and D.B. Zax.

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