

# Polymer Layered Silicate Nanocomposites\*\*

By Emmanuel P. Giannelis\*

Polymer nanocomposites with layered silicates as the inorganic phase (reinforcement) are discussed. The materials design and synthesis rely on the ability of layered silicates to intercalate in the galleries between their layers a wide range of monomers and polymers. Special emphasis is placed on a new, versatile and environmentally benign synthesis approach by polymer melt intercalation. In contrast to *in-situ* polymerization and solution intercalation, melt intercalation involves mixing the layered silicate with the polymer and heating the mixture above the softening point of the polymer. Compatibility with various polymers is accomplished by derivatizing the silicates with alkyl ammonium cations via an ion exchange reaction. By fine-tuning the surface characteristics nanodispersion (i.e. intercalation or delamination) can be accomplished. The resulting polymer layered silicate (PLS) nanocomposites exhibit properties dramatically different from their more conventional counterparts. For example, PLS nanocomposites can attain a particular degree of stiffness, strength and barrier properties with far less inorganic content than comparable glass- or mineral reinforced polymers and, therefore, they are far lighter in weight. In addition, PLS nanocomposites exhibit significant increase in thermal stability as well as self-extinguishing characteristics. The combination of improved properties, convenient processing and low cost has already led to a few commercial applications with more currently under development.

## 1. Introduction

Composites are already widely used in such diverse areas as transportation, construction, electronics and consumer products. They offer unusual combinations of stiffness, strength, and weight that is difficult to attain separately from the individual components. Nanocomposites, on the other hand, are a relatively new class of materials with ultrafine phase dimensions, typically of the order of a few nanometers.<sup>[1-4]</sup> Because of their nanometer size features nanocomposites possess unique properties typically not shared by their more conventional microcomposite counterparts and, therefore, offer new technology and business opportunities.

At Cornell we have focused on the design and synthesis of polymer-ceramic nanocomposites with layered silicates as the inorganic phase (shown schematically in Fig. 1).<sup>[5-13]</sup> Our approach exploits the ability of layered silicates to intercalate between their layers a wide variety of monomers or polymers.<sup>[14,15]</sup> A particularly attractive design involves individual silicate layers (1 nm thick) homogeneously dispersed in a continuous polymer matrix (Fig. 1b) first developed by the Toyota group.<sup>[16-19]</sup> These polymer-layered silicate (PLS) nanocomposites can attain a certain degree of stiffness, strength and barrier properties with far

less ceramic content than comparable glass- or mineral-reinforced polymers. As such they are far lighter in weight than conventionally filled polymers.

Due to the layer orientation, polymer-silicate nanocomposites also exhibit stiffness, strength and dimensional stability in two dimensions (rather than one). In addition, because of the length scale involved that minimizes scattering, nanocomposites are usually transparent. Furthermore, PLS nanocomposites exhibit a significant increase in thermal stability as well as self-extinguishing characteristics.

Since PLS nanocomposites achieve composite properties at 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 they can be processed by techniques like extrusion, injection molding and casting normally reserved

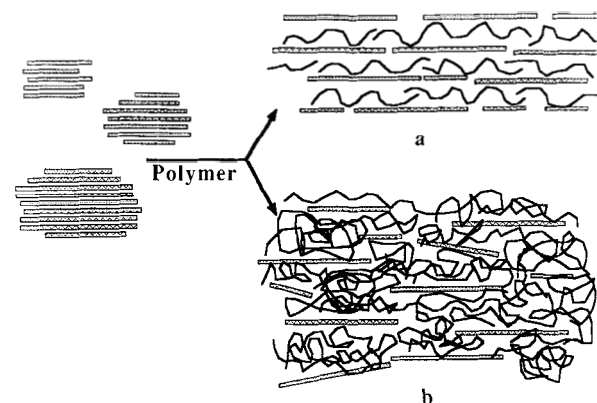


Fig. 1. Schematic of composite structures obtained using layered silicates. The rectangular bars represent the silicate layers. a) Single polymer layers intercalated in the silicate galleries (*intercalated hybrids*). b) Composites obtained by delamination of the silicate particles and dispersion in a continuous polymer matrix (*delaminated hybrids*).

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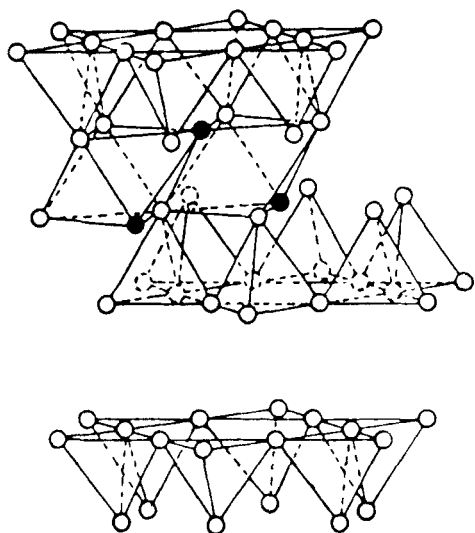


Fig. 2. Idealized structure of 2:1 layered silicates showing two tetrahedral-site sheets fused to an octahedral-site sheet. Open circles represent oxygens; shaded circles are hydroxyls. The galleries in the pristine silicates are usually occupied by hydrated alkali metal cations.

for unfilled polymers. Furthermore, they are adaptable to films, fibers as well as monoliths.

The combination of enhanced properties, weight reduction and low cost has already led to a few commercial applications. Toyota Motor Company has successfully introduced an automotive timing-belt cover made from a Nylon-layered silicate nanocomposite.<sup>[19]</sup> Ube Industries in Japan in collaboration with Toyota is also developing nanocomposite barrier films for food packaging and other applications. Similar R&D efforts focusing on silicate nanocomposites are already underway in several US companies. Potential applications include airplane interiors, fuel tanks, components in electrical or electronic parts, under-the-hood structural parts, brakes and tires.

## 2. Structure and Properties of 2:1 Layered (Mica-type) Silicates

The silicates used in PLS nanocomposites, like the better known members of the group talc and mica, belong to the

general family of 2:1 layered- or phyllosilicates. Their crystal structure consists of layers made up of two silica tetrahedra fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Fig. 2). 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 space. Although in pristine layered silicates the interlayer cations are usually hydrated  $\text{Na}^{\oplus}$  or  $\text{K}^{\oplus}$ , ion exchange reactions with various organic cations (e.g. alkylammonium cations, cationic surfactants etc.) render the normally hydrophilic silicate surface organophilic. The organic cations lower the surface energy of the silicate surface and improve wetting with the polymer matrix. Organosilicates are thus much more compatible with most engineering plastics. Additionally, the organic cations may contain various functional groups that react with the polymer to improve adhesion between the inorganic phase and the matrix.

There are two particular characteristics of layered silicates that we exploit in PLS nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. As a result an aspect ratio as high as 1000 for fully dispersed individual layers can be obtained. (Contrast that to an aspect ratio of about 10 for undispersed or poorly dispersed particles). The second characteristic, is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion in a given matrix, that, in turn, determines aspect ratio, depends on the interlayer cation.

Any physical mixture of a polymer and silicate (or inorganic material in general), however, does not form a nanocomposite. The situation is analogous to polymer blends. In most, separation into discrete phases normally takes place. In immiscible systems, that typically correspond to the more conventionally filled polymers, the poor physical attraction between the organic and the inorganic components leads to poor mechanical properties. Furthermore, particle agglomeration tends to reduce strength and produce weaker materials. In contrast, favorable interactions between the polymer and the silicate in PLS nanocomposites lead to the organic and



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inorganic phases being dispersed at the nanometer level. As a result nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers.

### 3. Nanocomposite Synthesis and Characterization

As you will recall from Figure 1 there are two possible types of nanocomposites with ultrafine dispersion: a) *intercalated hybrids* in which a single, extended polymer chain is intercalated between the silicate host layers resulting in a well ordered multilayer with a repeat distance of a few nanometers, and b) *delaminated hybrids* in which the silicate layers are exfoliated and dispersed in a continuous polymer matrix. In the latter the interlayer expansion is comparable to the radius of gyration of the polymer rather than that of an extended chain as in the case of intercalated hybrids. Thus, we can distinguish between undispersed or immiscible hybrids corresponding to conventional or macrocomposites and miscible or molecularly dispersed hybrids corresponding to either intercalated or delaminated systems. Furthermore, intercalated hybrids may be thought of as systems with limited miscibility compared to delaminated hybrids that show practically unlimited solubility.

Synthesis of PLS nanocomposites has typically involved either intercalation of a suitable monomer followed by polymerization (*in-situ* polymerization)<sup>[5-11,16-21]</sup> or polymer intercalation from solution.<sup>[5,14,22-24]</sup> Various mono- and multifunctional monomers have already been used, yielding linear and cross-linked polymer matrices, respectively. Alternatively, a polymer solution can be used.

For most technologically important polymers, both *in-situ* polymerization and intercalation from solution are limited because neither a suitable monomer nor a compatible polymer-silicate solvent system is always available. We have recently discovered a more versatile and environmentally benign approach based on direct polymer melt intercalation.<sup>[12,13]</sup> The process involves mixing the layer silicate with the polymer and heating the mixture above the softening point of the polymer.

Intercalation of poly(ethylene oxide), PEO, for example is accomplished by heating the polymer with the host at 80 °C.<sup>[13]</sup> Figure 3 shows the XRD pattern of PEO/Na<sup>+</sup>-montmorillonite hybrid before heating and after two and six hours at 80 °C, respectively. The X-ray pattern before any heating contains peaks characteristic of both pristine silicate ( $d = 1.14$  nm) and crystalline PEO (0.46, 0.38 and 0.32 nm). After heating to 80 °C, the intensity of the peaks corresponding to the un-intercalated silicate and crystalline PEO is progressively reduced while a set of new peaks appears corresponding to the PEO-intercalated silicate. After six hours, only reflections corresponding to the PEO-intercalated silicate are observed signifying the completion of intercalation. The  $d$ -spacing of 1.77 nm is identical to that

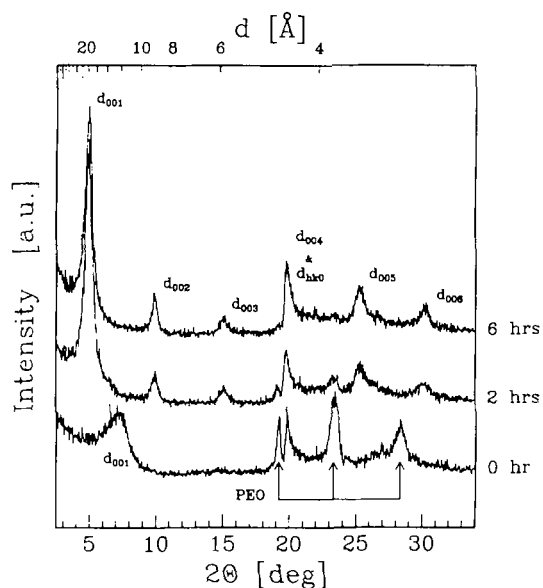


Fig. 3. X-ray diffraction pattern of PEO/Na<sup>+</sup>-montmorillonite hybrid heated to 80 °C for 0, 2 and 6 hours. From [13].

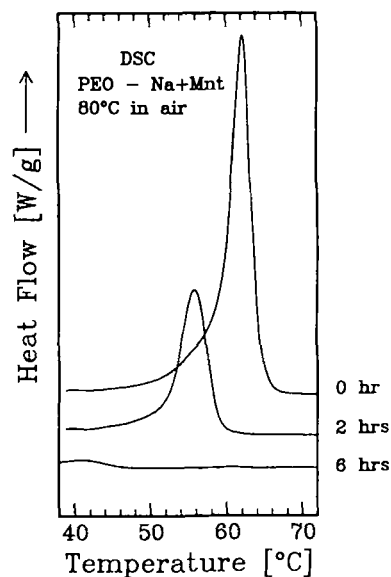


Fig. 4. DSC traces for PEO/Na<sup>+</sup>-montmorillonite hybrids heated to 80 °C for 0, 2 and 6 hours. From [13].

previously obtained for PEO intercalation from solution found by us and others.<sup>[5,22-24]</sup>

Differential scanning calorimetry (DSC) studies offer further evidence for intercalation. Figure 4 compares the DSC traces of PEO/Na<sup>+</sup>-montmorillonite after 0, 2 and 6 hours at 80 °C. Both the 0 and 2 hour traces clearly show a distinct endotherm corresponding to the melting transition of crystalline PEO. As the intercalation reaction progresses, more PEO chains are intercalated and the area of the endotherm corresponding to the crystalline PEO is reduced. After six hours, the transition has largely vanished suggest-

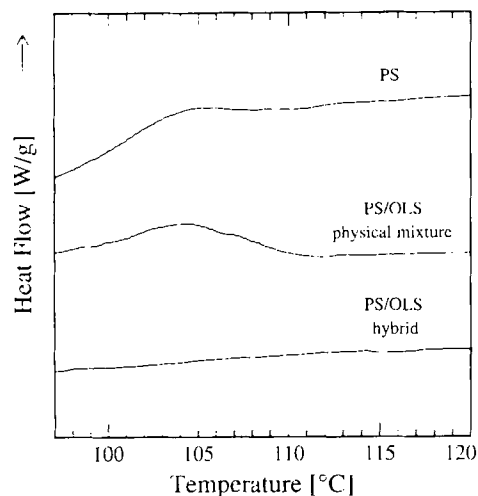


Fig. 5. DSC traces of pure PS, a physical mixture of PS-organosilicate and PS intercalated organosilicate. The ratio of silicate to PS in the physical mixture is the same as that for the intercalated hybrid. OLS stands for organosilicate.

ing that all the PEO is intercalated – consistent with the X-ray diffraction data that shows only reflections corresponding to the PEO intercalated phase. The shallow hump in the six hour trace is most likely due to a small fraction of un-intercalated crystalline polymer adsorbed on the external surfaces of the host particles.

In contrast to PEO, polystyrene, PS, will not intercalate in pristine silicates. However, intercalation does take place when an organosilicate such as dimethyltallow-exchanged montmorillonite is used.<sup>[12]</sup> (tallow, is composed predominantly of octadecyl chains with smaller amounts of lower homologues. The approximate composition is C<sub>18</sub> 70 %, C<sub>16</sub> 25 %, C<sub>14</sub> 4 % and C<sub>12</sub> 1 %). The resulting gallery height increase of 0.7 nm corresponds to a monolayer of nearly collapsed polymer chains.

Further evidence of PS intercalation is obtained by DSC. The DSC traces indicate also that the behavior of the intercalated PS is qualitatively different from that characteristic of the bulk polymer. Figure 5 shows DSC traces for pure PS, PS organosilicate mixture and PS intercalated organosilicate. The physical mixture contains the same polymer to silicate ratio as the intercalate. Both the pure polymer and the physical mixture of PS organosilicate clearly exhibit the characteristic glass transition at 96 °C but the intercalated hybrid does not.

In addition to PEO and PS polymers have included polyamides, polyesters, polycarbonate, polyphosphazene<sup>[25]</sup> and polysiloxanes.<sup>[26]</sup> Interestingly, polymer melt intercalation does not only lead to intercalated hybrids. For example, delaminated hybrids are obtained by suspending a dimethyltallow ammonium-exchanged montmorillonite in polydimethylsiloxane, PDMS, at room temperature and sonicating for two minutes. Elastomeric nanocomposites are finally obtained after cross-linking by adding tetraethylorthosilicate and tin-2-ethylhexanoate to the mixture and allowing to cure at room temperature.

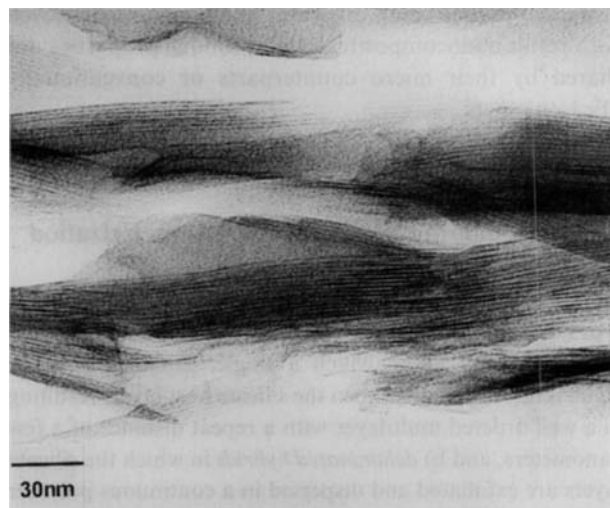


Fig. 6. Bright field TEM micrograph of a polystyrene silicate nanocomposite showing the coherent stacking of silicate layers as alternating dark lines.



Fig. 7. TEM micrograph of a cross-section of silicate epoxy nanocomposite containing 4 vol. % silicate. From [10].

In addition to XRD, the hybrids have been characterized by transmission electron microscopy, TEM. Figure 6 is a micrograph of a polystyrene layered silicate intercalated hybrid. The dark lines are the silicate layers separated by about 3 nm in agreement with the *d*-spacing observed by XRD. In contrast in delaminated hybrids we find single silicate layers embedded in the polymer matrix. A micrograph of an epoxy nanocomposite containing 4 vol. % silicate is shown in Figure 7. Well-dispersed individual silicate layers (dark lines in the figure) of thickness 1 nm are embedded in the epoxy matrix.

#### 4. Nanocomposite Properties

The advantages of hybrids containing single silicate layers uniformly dispersed in a polymer matrix were first demonstrated by a group at the Toyota Research Center in Japan for Nylon nanocomposites.<sup>[16-19]</sup> Table 1 summarizes and

Table 1. Properties of Nylon-6 and layered silicate Nylon nanocomposites [17].

Property	Nanocomposite	Nylon-6
Tensile Modulus (GPa)	2.1	1.1
Tensile Strength (MPa)	107	69
Heat Distortion Temp (°C)	145	65
Impact Strength (kJ/m <sup>2</sup> )	2.8	2.3
Water Adsorption (%)	0.51	0.87
Coefficient Thermal Expansion (x,y)	$6.3 \times 10^{-5}$	$13 \times 10^{-5}$

contrasts the properties of a Nylon nanocomposite containing 4 wt. % silicate to those of unfilled Nylon. Interestingly, the substantial increases in strength and modulus are not accompanied by a decrease in impact resistance as is usually the case with filled polymers. More importantly the heat distortion temperature of the nanocomposite is more than double, extending the use of Nylon to under-the-hood structural parts in the engine compartment. Note also the significant reduction in water adsorption for the nanocomposite.

Silicate-epoxy nanocomposites prepared in our group also show a similar improvement in mechanical properties.<sup>[10]</sup> For example, a nanocomposite containing 4 vol. % silicate shows a 60 % increase in storage modulus in the glassy region compared to the unfilled epoxy. The equivalent increase in the rubbery region is 450 %. This increase in modulus is quite remarkable, since conventionally filled epoxies with  $\mu\text{m}$  or larger size particles do not show much of an improvement in modulus at the loading levels (< 10 vol. %) used in the nanocomposites.

In recent work, Pinnavaia and co-workers have also shown that the modulus and strength of epoxy nanocomposites with sub-ambient glass transition temperatures show a more than 10-fold improvement.<sup>[21]</sup> This improvement was attributed to a possible strain-induced alignment of the silicate layers in the rubbery state.

Owing to our interest in developing materials with improved barrier properties, we have also studied the permeability of liquids and gases in the nanocomposites.<sup>[11]</sup> Figure 8 shows the relative permeability (permeability of the composite/permeability in the unfilled polymer,  $P_c/P_0$ ) of water as a function of silicate content. The permeability in the nanocomposite is dramatically reduced compared to the unfilled polymer. Also note how the decrease in permeability is much more pronounced in the nanocomposites compared to the conventionally filled polymers with much higher filler content. The dramatic reduction of permeability in the nanocomposites is due to the presence of dispersed large aspect ratio silicate layers in the polymer matrix which are impermeable to water molecules. This forces solutes traversing the

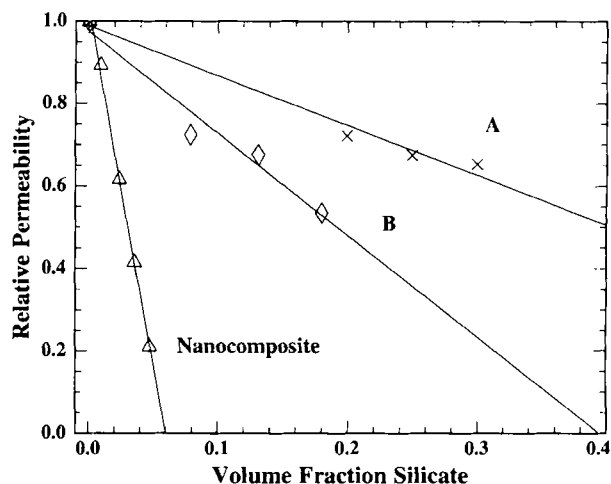


Fig. 8. Relative permeability,  $P_c/P_0$ , as a function of filler content for polycaprolactone nanocomposites and conventionally filled silicate composites (A,B).

film to follow a tortuous path through the polymer matrix surrounding the silicate particles, thereby increasing the effective path length for diffusion.

Nanocomposites also exhibit significant increases in heat resistance and thermal stability. For example, a polydimethylsiloxane nanocomposite shows a delayed decomposition compared to the unfilled polymer.<sup>[26]</sup> PDMS is well-known to decompose into volatile cyclic oligomers. Since the permeability of the nanocomposites is dramatically decreased, we attribute the increased thermal stability to hindered out-diffusion of the volatile decomposition products.

Furthermore, in preliminary tests we have found that nanocomposites containing no other additives exhibit self-extinguishing characteristics (Fig. 9). Both the unfilled polymer and the nanocomposite were exposed to an open flame for about 30 s. The nanocomposite ceased burning after the flame was removed, retaining its integrity. In contrast, the unfilled polymer persisted burning leading to specimen destruction. In the nanocomposites the silicate layers act most likely as

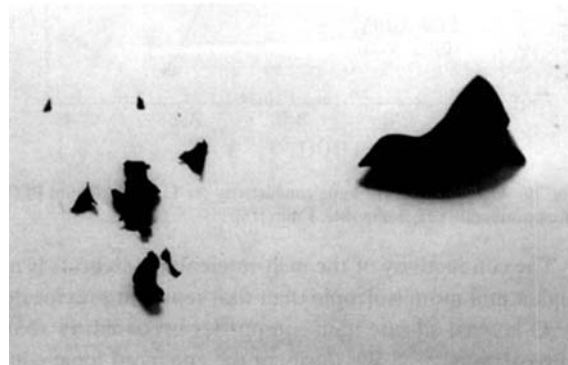


Fig. 9. Nanocomposite containing 7.5 vol. % silicate (on the right) and unfilled polycaprolactone (left) after being exposed to an open flame for 30 s.

barriers inhibiting gaseous products from diffusing to the flame and shielding the polymer from the heat flux. As more heat, produced from further oxidation of volatiles in the gas phase, is fed back into the polymer, further breakdown of the polymer takes place. In the nanocomposites this self-sustaining cycle is suppressed leading to self-extinguishing characteristics.

Lastly, we demonstrate the potential of nanocomposites as alternatives to polymer electrolytes. A serious drawback in PEO electrolytes has been the precipitous decrease of conductivity (from  $10^{-4}$  to  $10^{-8}$  S/cm) below their melting temperature.<sup>[27]</sup> This decrease is due to the formation of crystallites that severely impede ionic mobility. Since intercalation impedes polymer crystallization, it can potentially enhance the electrolyte conductivity. Additionally, since the counter anions in the nanocomposites are the comparatively immobile silicate layers, single-ion conductor behavior is anticipated.

An Arrhenius plot of the in-plane ionic conductivity of the PEO/Li<sup>+</sup>-montmorillonite nanocomposite containing 40 wt. % polymer is shown in Figure 10. For comparison, the conductivity of a conventional LiBF<sub>4</sub>/PEO electrolyte with a comparable O/Li ratio is also shown.<sup>[13]</sup> As expected, the conductivity of the LiBF<sub>4</sub>/PEO electrolyte decreases several orders of magnitude below the melting temperature. In contrast, the conductivity of the nanocomposite exhibits only a weak temperature dependence over the same temperature range. In addition, the apparent activation energy in the nanocomposite (2.8 kcal mol<sup>-1</sup>) is similar to that of the molten polymer electrolyte suggesting that the mobility of Li<sup>+</sup> in the nanocomposites is comparable to that in the bulk molten electrolyte.

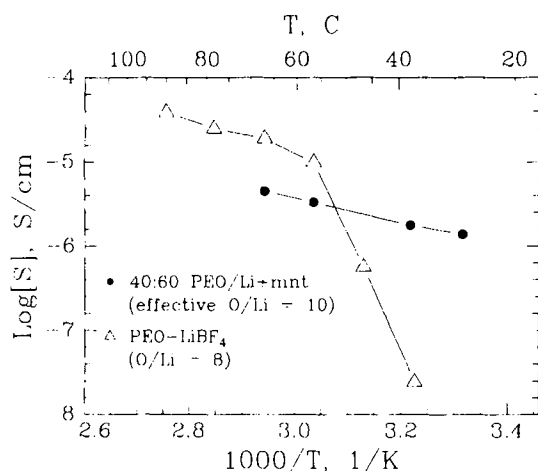


Fig. 10. Arrhenius plots of ionic conductivity for LiBF<sub>4</sub>/PEO and PEO/Li<sup>+</sup>-montmorillonite nanocomposite. From [13].

The conductivity of the melt-intercalated hybrids is much higher and more isotropic than that reported previously for PEO/layered silicate nanocomposites prepared by solution intercalation.<sup>[22-24]</sup> We attribute the enhanced ionic conductivity in our samples to the presence of excess polymer that provides an easy conduction path between host particles.<sup>[13]</sup>

## 5. Miscibility Issues/Thermodynamics of Hybrid Formation

Most of the work to date has focused on nanocomposite synthesis and property evaluation. To optimize the properties of the hybrids, develop predictive capabilities to the range of polymer-silicate systems, and design silicates which are miscible (or compatible) with different polymer matrices a number of questions first need to be addressed. For example, why do certain polymer-silicate systems favor intercalated hybrids, others delaminated and yet others are immiscible leading to macrocomposites? How does packing density and chain length of the alkylammonium chains in the organosilicates, layer charge of the silicate or specific groups on the polymer (or the alkyl chains) affect hybrid formation and miscibility? How does temperature or shear affect processing? And finally, how does the type of bonding at the polymer/silicate interface (i.e. hydrogen, dipole-dipole, van der Waals or covalent in which the alkylammonium chains become part of the polymer chain) affect the properties of the hybrid?

To address some of these questions and delineate the factors favoring intercalated vs. delaminated hybrids we have already initiated an effort focusing on the thermodynamics governing nanocomposite formation. To that end we are developing a mean-field, lattice-based thermodynamic model.<sup>[25]</sup> Assuming the configurations and interactions of the various constituents are independent, the free energy change of hybrid formation is separable into independent enthalpic and entropic terms. The entropic term is, then, the sum of the configurational changes associated with the polymer and the silicate (including the alkyl ammonium chains in organosilicates). Configurational changes of the silicate are determined using a modified Flory-Huggins lattice model in which the occupation of the lattice is weighted to simulate the preferred orientations of the alkylammonium cations in the presence of two impenetrable surfaces (silicate layers). The confinement of the intercalated polymer chains is similarly approximated using a self-consistent field treatment of a random-flight polymer with excluded volume between two surfaces. For the enthalpic term a modified mean-field, site-fraction approach where the number of contacts per lattice site is replaced by an interaction area per lattice site is being used. This modified approach allows one to express the interaction parameter as energy per area and may be approximated by interfacial or surface energies.

The following summarizes our initial calculations.<sup>[25]</sup> The entropy loss associated with polymer confinement that ordinarily inhibits intercalation must be compensated by entropy gains associated with the layer separation. If the entropy loss is larger or in the best case scenario about equal to the entropy gain, enthalpy will determine whether or not intercalation will take place. Ideally, polymers should be polar or contain groups capable of interacting with the silicate surface. If the enthalpy cannot compensate for the

entropy penalty no intercalation will take place leading to undispersed or immiscible hybrids. As polymer silicate interactions become stronger first intercalated and then delaminated hybrids are predicted in agreement with our experimental observations.

## 6. Kinetics of Polymer Intercalation

Since the silicate particles are effectively agglomerates of smaller, primary particles consisting of 10–20 layers in a coplanar orientation (usually referred to as the tactoids), hybrid formation may be limited by two processes: diffusion of the polymer chains into the agglomerates or diffusion of the polymer chains within the silicate galleries. Using in-situ XRD experiments and TEM we have determined that hybrid formation is limited by mass transport into the silicate primary particles and not specifically by diffusion of the polymer chains within the silicate galleries.<sup>[25]</sup> The activation energy of hybrid formation is similar to that previously measured for polymer self-diffusion in the melt, implying that the diffusivity of the polymer chains within the host galleries is at least comparable to that in the melt. Therefore, hybrid formation requires no additional processing time than currently required by conventional polymer processing techniques such as extrusion.

## 7. Conclusions

We have presented several examples of polymer nanocomposites with layered silicates as the inorganic phase. The materials design and synthesis rely on the ability of layered silicates to intercalate in the galleries between their layers a wide range of monomers and polymers. Special emphasis is placed on a new, versatile and environmentally benign synthesis approach by polymer melt intercalation. In contrast to in-situ polymerization and solution intercalation, melt intercalation involves mixing the layer silicate with the polymer and heating the mixture above the softening point of the polymer. Compatibility with various polymers is accomplished by derivatizing the silicates with alkylammonium cations via an ion exchange reaction. By fine-tuning the surface characteristics nanodispersion (i.e. intercalation or delamination) can be accomplished.

The resulting polymer layered silicate nanocomposites exhibit properties dramatically different from their more conventional counterparts. For example, PLS nanocompo-

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