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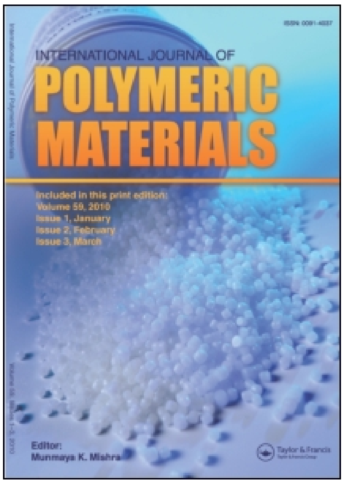

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Polymer Nanocomposites Based on Layer Aluminum-silicates

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The structure particular to layer aluminumsilicates is discussed permitting the intercalation of polymers. This process ultimately leads to nanocomposites that exhibit interesting properties. It will be shown that many improvements of physical properties can be achieved by polymer-clay nanocomposites.

Keywords: Aluminum silicates; structure; intercalation of polymers; clay-polymer nanocomposites; physical properties; polymer; nanocomposite; layer aluminum silicate; intercalation; clay; modulus; thermal expansion coefficient; permeability; solvent resistance; flammability.

INTRODUCTION

Nano-composites based on aluminum silicates can be obtained by intercalation. This process will take place if polar polymers or polymers containing groups capable of interacting with the silicate surface are brought into contact with the porous silicates.

These nanocomposites are a relatively new class of materials having ultrafine dimensions, typically of the order of a few nanometers. These materials are of great scientific importance, and it is expected that they will ultimately find significant use in many technological applications. The objectives of this overview is to present the current technical an scientific background related to these new materials.

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RESULTS AND DISCUSSION

A. Particular Structure of Layer Aluminum Silicates

The clay minerals are mainly hydrous aluminum silicates containing various amounts of magnesium and iron while alkali metals are essential constituents in some of them.

The structure of these silicates can be derived by combinations of a silicon oxygen sheet (a silica tetrahedron SiO_4, consisting of a silicon, Si^{+4}), surrounded by four oxygen atoms, with an octahedral sheet consisting of cations such as Al^{+3}, Mg^{+2}, Fe^{+3}, Fe^{+2}, *etc.*, surrounded by six hydroxyl groups. The simplest structure that can be derived in this way is that of the kaolinite group of clay minerals which are composed of a single octahedral sheet combined with a single tetrahedral sheet through the substitution of unshared apical oxygen atoms in the tetrahedral sheet for hydroxyl in the octahedral sheet to form a common layer structural unit.

The other major layer types group of which montmorillonite is an important member consists of combination of two tetrahedral sheets combined with a central octahedral sheet. The stacking of these layers is of such nature that a very weak bond exists between them. This property is responsible for the most important feature of the montmorillonite (smectite) structure in that water and other polar molecules can enter between the unit, layer, causing the lattice to expand (the so called swelling clays). The exchangeable cations are absorbed between the unit layers and around their edges in order to balance the charge deficiencies.

Clay minerals are highly reactive due to their large surface area and because they commonly carry a charge usually due to ionic substitution in the tetrahedral and octahedral sheets. The existence of the charge is the basis for the exchange capacity and the swelling properties which are both extremely important to the civil engineer.

The cation-exchange capacity of a sheet silicate is itself a useful guide, qualitatively and quantitatively, as far as tendency to intercalate is concerned less [1]. The unit commonly used for this purpose is milliequivalents of interlamellar cation that may be exchanged per 100 g of silicate. For the micas (muscovite and phlogipite) the cation-exchange capacity is ca 250 mEq per 100 g; it is somewhat more (ca 270) for lepidolite, rather less for vermiculites (100 – 170), and a good deal less (60 – 120) for the smectites as a family. Again, the precise values depend on the extent and nature of the isomorphous substitution, which, in turn, is governed by the manner of synthesis, whether it be in nature or in the laboratory. As a rough rule, it is useful to bear in mind that montmorillonites posses a surplus electronic charge on their layers of ca 0,5 – 0,7 per formula unit.

A summary of the cation-exchange capacities, expressed in the conventional units of clay mineralogy, milliequivalents per 100 g, is given in Table I.

B. Techniques for Elucidating the Nature of Intercalated Clays

In this section we briefly and selectively cite the various techniques that are used to identify and characterize intercalated clays.

Simple measurements of the amount of guest species taken up by a host clay, especially when expressed in mole percent or as a fraction of the theoretically available interlamellar space, soon affords insights as to whether genuine intercalation has taken place.

Gravimetric methods particularly thermogravimetry in which both sorption and desorption can readily be monitored, quickly reveal whether intercalation, rather than just multilayer physical adsorption, is involved. X-ray diffraction is extremely helpful since there is usually an increase in the *c*-axis repeat distance (the inter-layer spacing) when organic molecules are taken up. This simple test, although generally reliable, can be misleading. There are now many instances in which it is know on other grounds that intercalation has indeed taken place but there is very little change in *d* spacing. A carefully recorded X-ray

TABLE I Typical magnitudes of the cation-exchange capacity of some sheet silicates

Sheet silicate	*Cation-exchange capacity (mEq/100 g)*
Kaolinite	3 – 15
Halloysite · $2H_2O$	5 – 10
Smectites	60 – 120
Vermiculites	100 – 170
Muscovite	252
Phlogopite	240

powder diffractometer trace, in which the intensities of each peak are readily seen, does, however, offer generally reliable information as to the occurrence of intercalation.

Having established that intercalation is a reality, several methods are then, in principle, available for more precise characterization.

1. Detailed X-ray and/or neutron diffraction studies may be performed on highly oriented specimens. These yield one-dimensional Fourier maps, from which the orientation of the guest molecule in the interlamellar space may be inferred. If the intercalate is very well ordered, it may be possible to record a full three-dimensional structure of the complex.
2. Infrared and other spectroscopic techniques, including X-ray-induced photoelectron spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis), X-ray photoelectron diffraction (XPD), Mössbauer spectroscopy, NMR, and ESR may also be invoked.
3. Electron microscopy may be used in certain cases. However these techniques are used to best advantage when a stable intercalate is formed. When chemical reactions occur freely within the micro-environment of the interlamellar region, it is difficult to monitor directly the changes that accompany, or illuminate the nature of the changes themselves. Frequently one simply monitors the product distribution or amount of converted reactant as a function of contact time with the clay intercalate.

C. Polymer Layered Silicate Nanocomposites

Ideally intercalation will take place if polymers is polar or contain groups capable of interacting with the silicate surface.

Nanocomposites are a relatively new class of materials with ultrafine phase dimensions, typically of the order of a few nanometers. The design and synthesis of polymer-ceramic nanocomposites with layered silicates as the inorganic phase are shown schematically in Figure 1 [2].

The transport pathways and mechanisms depend on the morphology and nanostructure of the layered host. The layer size, spatial distribution and defect structure will influence transport of polymer into the silicate interlayer, movement of the layers into the polymer bulk and the potential number of favorable polymer-silicate interaction sites.

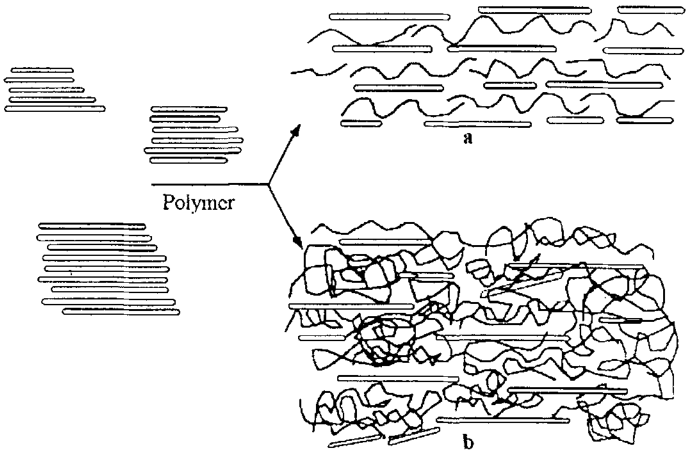


FIGURE 1 Schematic of composite structures obtained using layered silicates. The rectangular bars represent the silicate layers. (a) Single polymer layers intercalated in the silicate galleries (*intercalated hybrids*). (b) Composites obtained by delamination of the silicate particles and dispersion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

The ultrafine phase dimensions of nanocomposites, typically ranging between 1 and 10 nm, lead to new and improved properties when compared to their pure polymer constituent or their macro-composite counterparts. For example, polymer-silicate nanocomposites exhibit increased modulus [3 – 5], decreased thermal expansion coefficient [4, 6], reduced gas permeability [4, 6], increased solvent resistance [7] and enhanced ionic conductivity [8] when compared to the pristine polymers. These performance improvements, though, depend greatly on the distribution, arrangement, and interfacial bonding between the silicate layers and the polymer.

D. Preparation of Polymer-organically Modified Layered Silicates

Synthesis of polymer-organically modified layered silicates nanocomposites may be received by varied methods:

1. typically intercalation of suitable monomer followed by polymerization,
2. polymer intercalation from solution,
3. direct polymer melt intercalation.

The normally hydrophilic silicate surface complicates synthesis of polymer-organically modified layered silicates nanocomposites by any of above mentioned methods.

This problem may be removed by means of silicate surface modification. Isomorphic substitution within the layers generates negative charges that are normally counterbalanced by cation residing in the interlayer space. Although in pristine layered silicates the interlayer cations are usually hydrated Na^+ or K^+, ion exchange with various organic cations (*e.g.*, alkylammonium cations, 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.

E. Modified Organophilic Clays and their Preparation

In the work [16] was researched organophilic modification of montmorillonite by some organic materials. Organophilic clays were prepared in the form of disperse in organic solvents. However montmorillonite is too hydrophilic to disperse in organic solvents. The hydrophilicity of montmorillonite should be reduced to allow dispersion in organic solvents. As montmorillonite has an excess negative charge, it can be combined with organic cations to yield organophilic montmorillonite intercalated with organic cations.

Table II shows the dispersibility of organophilic montmorillonites in dimethylacetamide (DMAC) which is a solvent for preparation of polyimides and the average diameter of organophilic montmorillonites obtained from the dynamic light scattering experiment.

As the carbon number of the organic compound increases, the hydrophilicity of the organophilic montmorillonite decreases. Table II indicates that 10–20 carbons is appropriate for organophilic montmorillonite to be dispersed in DMAC. Longer carbon chains make organophilic montmorillonite too hydrophobic.

Organophylic Na-montmorillonite was obtained by a cation-exchange reaction between Na-montmorillonite and the distearyldimethylammonium ion, and its organic content was 47 wt.% [10].

TABLE II Average diameter of intercalated montmorillonites in DMAC

Intercalated species	*Dispersibility of DMAC dispersion*[a]	*Average diameter*[b] *(μm)*
n-Octyltrimethylammonium chloride	X	–
Ammonium salt of dodecylamine	O	0.44
Ammonium salt of 12-aminododecanoic acid	Δ	3.75
n-Dodecyltrimethylammonium chloride	Δ	0.61
n-Dodecyltrimethylammonium chloride	X	–
n-Hexadecyltrimethylammonium chloride	X	–
n-Dioctadecyldimethylammonium chloride	X	–
n-Trioctylmethylammonium chloride	X	–
n-Benzyltrimethylammonium chloride	X	–

[a] It was judged by the appearance of DMAC dispersion of organophilic montmorillonite: (O) dispersible, (Δ) partly dispersible, (X) not dispersible.

[b] Values of average diameter are much bigger than 2000 Å, because an average diameter from light scattering measurement includes solvent around a substance.

Organically modified layered fluorohectorites were synthesized by cation-exchange reaction between Li-fluorohectorite and octadecylamine and dodecylamine, respectively [11].

Authors of patent [12] obtained vermiculite mineral species of intercalated cations selected from the group consisting of lithium, (C_2-C_6 alkyl) ammonium, allylammonium, or ammonium C_3-C_6 alkyl carboxylic acid.

An organophilic smectite-type clay were synthesized by intercalation of organic matters consisting of a β, γ-unsaturated alkyl group, a hydroxyalkyl group having 2 to 6 carbon atoms, a long chain alkyl group having 12 to 60 carbon atoms, an aralkyl group, phosphorous and nitrogen [13].

F. Monomer Modified Layered Silicates Nanocomposites, their Polymerization and Polymer Properties

This problem was examined in works which leading by Giannelis [14–20, 21–24]. For example a poly(ε-caprolactone)-layered silicate nanocomposite has been synthesized by Messersmith and Giannelis [25]. Preliminary the organically modified mica-type silicate (OMTS) was synthesized by an ion exchange reaction between Na-montmorillonite and a protonated amino acid as depicted in Eq. 1:

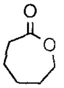
$$Na^+ - MTS + HO_2CRN^+H_3Cl^- HO_2CRN^+H_3 - MTS + NaCl \quad (1)$$

Then poly(ε-caprolactone)-silicate nanocomposites (PCLC) were synthesized by mixing 0 to 30% by weight of OMTS with ε-caprolactone in a vial at room temperature for 1 to 2 h followed by heating in an oil bath with stirring at 170°C for 48 h. At the end of the reaction, the vials were cooled to room temperature and the solidified product was recovered by breaking the glass vials.

A protonated amino acid was 12-aminolauric acid. The choice of 12-aminolauric acid, in addition to improving silicate delamination, was also motivated by the potential of the carboxylic groups to initiate polymerization of ε-caprolactone.

Acid groups ionically bound to the silicate layers at the protonated amine terminus can act as nucleophiles, reacting with ε-caprolactone as shown below:

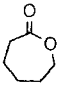
$$\mathrm{MTS\text{-}H_3\,N^+\,RCO_2H} \;+$$



$$\longrightarrow \quad \mathrm{MTS\text{-}H_3N^+RCO_2C(=O)(CH_2)_5OH} \qquad (2)$$

Then poly(ε-caprolactone) resulted according to ed. [3]

$$\mathrm{MTS\text{-}H_3N^+RCO_2C(=O)(CH_2)_5OH} \;+ n$$



$$\longrightarrow \quad \mathrm{MTS\text{-}H_3N^+RCO_2[C(=O)(CH_2)_5OH]_{n+1}H} \qquad (3)$$

It is important to point out that the resulting PCL chains are ionically bound to the dispersed mica-type silicate (MTS) layers through the protonated amine terminus of the polymer, which restricts chain mobility.

In order to release the polymer from the silicate surface the ammonium terminated PCL chains attached to the silicate layers are replaced by Li^+ as shown in Eq. (4).

$$\mathrm{MTS - H_3N^+RCO_2[C(=O)(CH_2)_5O]_{n+1}H + LiCl \longrightarrow Cl^-H_3N^+RCO_2[C(=O)(CH_2)_5O]_{n+1}H + Li^+ - MTS} \qquad (4)$$

The consequence of this reaction is the agglomeration (flocculation) of Li$^+$ –MTS into large multilamellar particles, allowing separation of the polymeric and silicate phases of the nanocomposite by sedimentation or centrifugation.

The onset of polymer melting in the nanocomposites was found to vary with silicate loading as shown in Figure 2. Specifically the onset melting temperature of the nanocomposites was found to vary from 57.0°C (PCLC1) to 53.5°C (PCLC20). This behavior coordinates with the effect of MTS loading on PCL crystal size (*i.e.*, smaller crystallite size is reflected in lower melting temperatures).

Molecular weight data derived from GPC experiments on polymer recovered according to Eq. (4) are listed in Table III. There is a general trend toward lower PCL molecular weight with increasing OMTS

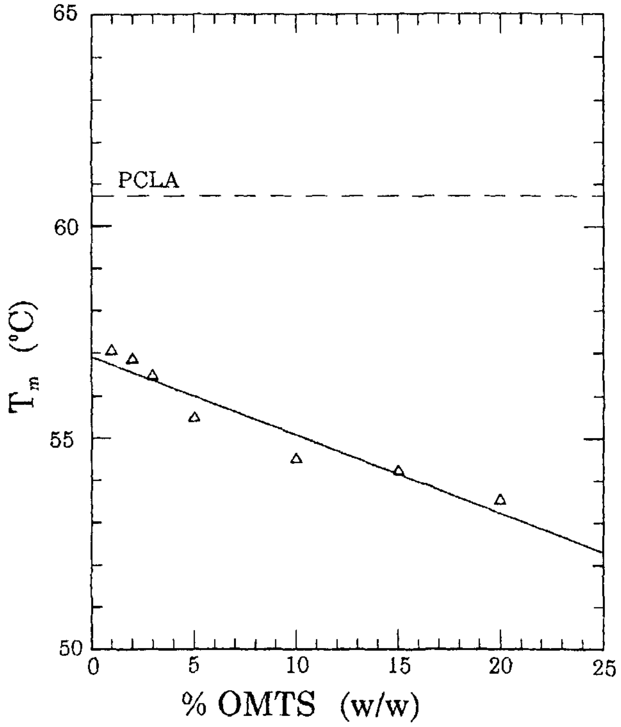


FIGURE 2 Plot of the temperature of onset of polymer melting *versus* weight fraction of OMTS in the PCLC nanocomposites. Dashed line corresponds to the melting temperature of PCLA.

TABLE III Molecular weights of recovered poly(ε-caprolactone)

Sample	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
PCLC1[a]	30,940	17,160	1.80
PCLC2	16,880	10,280	1.64
PCLC3	14,470	9,240	1.57
PCLC5	13,550	8,790	1.54
PCLC10	16,030	9,850	1.63
PCLC15	13,430	8,520	1.57
PCLC20	12,290	7,900	1.55

[a] Number at end of acronym indicates weight % OMTS in the composite.

content in the PCLC nanocomposites. This observation is consistent with the notion that the organic acid groups in the OMTS initiate ring-opening polymerization of Cl during synthesis of the nanocomposite. Thus, increasing the OMTS concentration effectively increases the initiator concentration, which reduces polymer molecular weight. It is possible that the reduction in PCL molecular weight can be responsible in part for the observed melting point depression with increasing silicate content (Fig. 2)

Also authors of works [25] has studied the permeability of water in PCLC nanocomposite films. Shown in Figure 3 are plots of the amount of weight gain of the nanocomposite film/desiccator apparatus. Under steady state conditions the increase in weight with time corresponds to the amount of water diffusing through the nanocomposite films.

Water vapor permeabilities calculated from the data in Figure 3 are tabulated in Table IV. Interestingly the permeability of the nanocomposite was reduced by nearly an order of magnitude at only 4.8% silicate by volume.

The solvent casting technique used here to form the nanocomposite films can result in in-plane orientation of the silicate layers which are impermeable to water molecules. This forces solutes traversing the film to follow a tortuous path through the polymer matrix surrounding the silicate particles, thereby increasing the effective path length for diffusion.

The observed dramatic decrease in water permeability is of great importance in evaluating PCL and PCL composites for use in food packaging, protective coatings, and other applications where efficient polymeric barriers are needed. For these applications significant

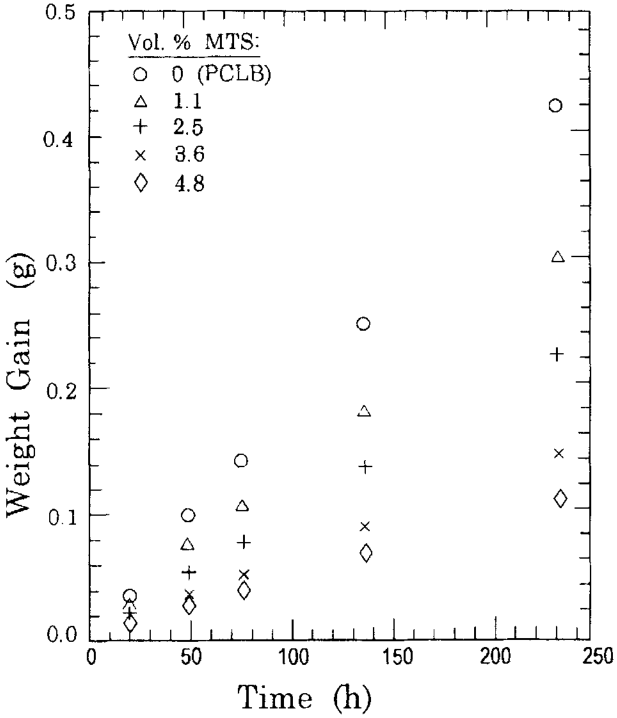


FIGURE 3 H_2O weight gain of nanocomposite film-covered dessicators *versus* exposure time in a 75% relative humidity almosphere. Data for nanocomposite films containing .011, .025, .036, and .048 volume fraction silicate are shown.

TABLE IV Composition and water vapor permeability of nanocomposite films

g PCLB	*g PCLC* 15	*Vol %* *silicate*	*Permeability* (10^{-3} $g \cdot m/h \cdot m^2$)
4.0	0.0	0.0	.185±.023
3.2	0.8	1.1	.164±.011
2.4	1.6	2.5	.113±.017
1.6	2.4	3.6	.076±.003
0.8	3.2	4.8	.038±.006

reduction in permeability can result in either increased barrier efficiency, or reduced thickness of the barrier layer for the same efficiency. Furthermore, reduced water permeability in biodegradable polymer composite films may have the added benefit of modifying degradation rates, because hydrolysis of matrix polymer is likely to depend on transport of water from the surface into the bulk of the material. In the work [2] authors reports about research flammability of PCLC nanocomposite samples. Both the unfilled PCL and 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 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.

Also a penetration of monomer in layered silicates may be realizated by using monomer solution. For example authors work [26] synthesised polyimide layered silicate nanocomposite. Synthesis realizated by interaction of monomer or prepolymer solution with layered silicates. Then solvent are removing. After that sample are polymerized. Owing to the intercalated clay mineral, the composite material has improved gas and water vapor barrier properties and a small thermal expansion coefficient.

The polyamide silicate nanocomposite was received [27] by interaction of a composite having the organic cation of the lactam adsorbed on to the layered silicate with a polyamide monomer. Then mixture containing the polyamide monomer is polymerized to prepare the polyamide composite material.

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 [21–24]. Table V summarizes and contrasts the properties of a nylon nanocomposite containing 4 wt.% silicate to those of unfilled nylon [22].

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.

TABLE V Properties of nylon-6 and silicate-nylon nanocomposites

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^2)	2.8	2.3
Water adsorption (%)	0.51	0.87
Coefficient thermal Expansion (x, y)	$6.3 \cdot 10^{-5}$	$13 \cdot 10^{-5}$

Note also the significant reduction in water adsorption for the nanocomposite.

Silicate-epoxy nanocomposites prepared by Messersmith and Giannelis [19] also show a similar improvement in mechanical properties. 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 μm or larger size particles do not show much of an improvement in modulus at the loading levels < 10 vol.% used in the nanocomposites.

In the work [28] Pinnavaia and coworkers have also shown that the modulus and strength of epoxy nanocomposites with sub-ambient glass transition temperatures show a more than 10-fold improvement. This improvement was attributed to a possible strain-induced alignment of the silicate layers in the rubbery state.

G. Polymer Modified Layered Silicates Nanocomposites and their Properties

In the work [9] a polyimide hybrid with montmorillonite clay mineral has been synthesized from a dimethylacetamide (DMAC) solution of poly(amic acid) and a DMAC dispersion of montmorillonite intercalated with an ammonium salt of dodecylamine. A mixture was stirred vigorously at 30°C for 5 h. Then the solution were spread and placed in a draft for 2 days to remove DMAC gradually. These samples were heated at 100°C for 1 h, at 150°C for 1 h, and at 300°C for 2 h under nitrogen atmosphere, yielding a 60 μm film of polyimide-clay hybrid.

Authors [9] researched series of physical quality showing polyimide hybrid with montmorillonite clay. Moisture absorption was measured by weight increase after placing the 60 μm polyimideclay hybrid film into water at 24°C for 3 days. Water vapor permeability coefficient was measured following ASTM E-96. The gas permeability coefficient of He and O_2 was measured using a Yanako GTR10. Thermal expansion coefficient parallel to the film surface direction was measured using DuPont TMA2940. Figures 4, 5, 6 accordingly show change of water vapor, O_2 and He-permeability *vs.* montmorillonite content.

As the content of montmorillonite in the polyimide-clay hybrid increases, the permeability coefficient of water vapor decreases remarkably. Only 2 wt.% addition of montmorillonite brings the permeability coefficient of water vapor to a value less than half of that of polyimide. The behavior for He and O_2 is almost the same as that of water vapor.

Montmorillonite content dependence of thermal expansion coefficients at various temperatures is shown in Figure 7. As the content of montmorillonite in the polyimide-clay hybrid increases, the thermal expansion coefficient decreases notably. If polyimide is used for electronics applications, it is important to match the thermal expansion

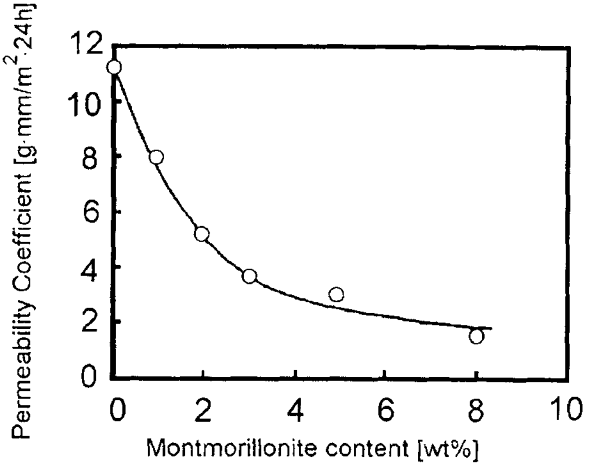


FIGURE 4 Montmorillonite content dependence of water vapor in polyimide-clay hybrid.

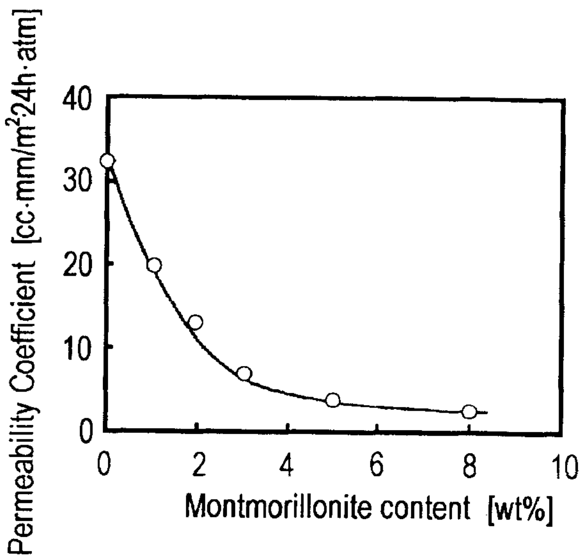


FIGURE 5 Montmorillonite content dependence of permeability coefficient of O_2 in polyimide-clay hybrid.

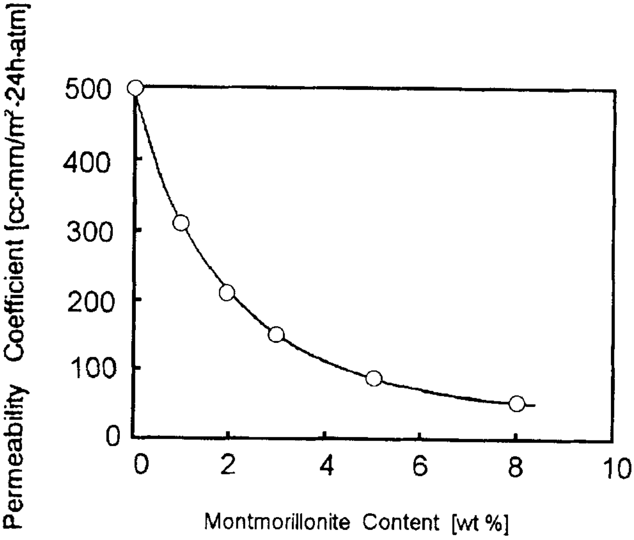


FIGURE 6 Montmorillonite content dependence of permeability coefficient of He in polyimide-clay hybrid.

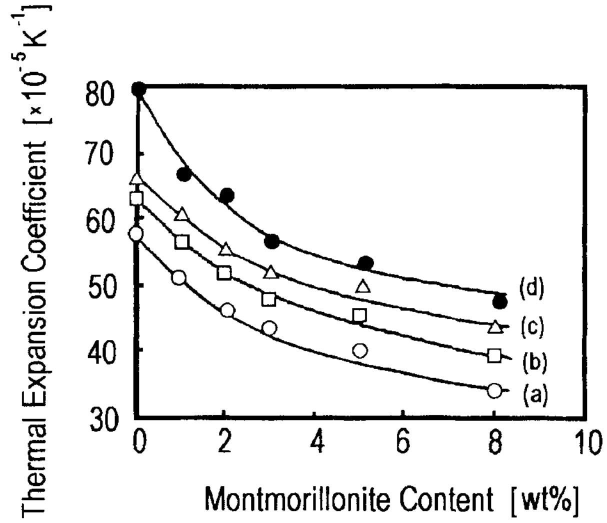


FIGURE 7 Montmorillonite content dependence of thermal expansion coefficient of polyimide-clay hybrid at: (a) 150°C, (b) 200°C, (c) 250°C, and 250°C.

TABLE VI Weight rests of thermodestruction of PVA-clays nanocomposites

Composition	*Weight rest, mg*	*Initial sample weight, mg*
PVA	7.5	90
Intercalated montmorillonite	7.2	10
Kaolinite	8.8	10
PVA + wt.% intercal.montmoril	20.0	100
PVA + wt.% kaolinite	21.5	100

Thermogravimetric analysis realized in air at heating velocity of samples 7°/min.

coefficient that of silicon substrate. This hybrid would be suited for such a use.

Authors this review synthesized polyvinyl alcohol-clay complexes using 10 wt.% water solution of polyvinyl alcohol (PVA). In this solution added clay which quantity equally 10 wt.% from quantity PVA. The composition was stirring and heating during 4 hr at 80°C. Then films were obtained which weight became constant by drying.

Thermogravimetric analysis of this samples (Tab. VI) showed increasing of weight rest at 500°C larger summary of PVA and clay rests. This result may be explained by difficulty of going out of PVA molecular fragments from layer gallery of clay and accordingly slowing of PVA thermo-destruction.

Authors researched flammability this films by Oxygen Index method. Results of samples Oxygen Index showed in Table VII.

Similar experiments was executed with montmorillonite intercalated by bis(dimethyl)bis(octadecyl) ammonium chloride. Experimental results of films containing PVA with 10 wt.% intercalated montmorilloonite are showed in Tables VI and VII. These results also may be explained by intercalation of PVA molecule fragments in the layer gallery the montmorillonite.

So far as intercalation of PVA molecule fragments in layer gallery of clay are accompanied by slowing of thermodestruction flammability of this compositions decreases and OI increases.

Polymer modified layered silicates nanocomposites may been formed by heating a mixture of polymer and layered silicate above the glass transition or melting temperature of the polymer [8, 29, 30].

In the work [31] authors synthesized a melt intercalated polystyrene-organically modified layered fluorohectorite. Organically modified layered silicate (octadecylammonium-exchanged fluorohectorite) and polystyrene (ratio 3:1 by weight) were mechanically mixed and formed into a pellet using a hydraulic press and a pressure of 70 MPa. Excess polymer was used to avoid polymer depletion during melt intercalation. The pellets were subsequently annealed in vacuum at temperatures greater than the glass transition temperature of the polystyrene.

The microstructure of the ordered intercalate investigated by using X-ray diffraction and transmission electron microscopy.

For the examining sample approximately 40% of the silicate interlayers contain polystyrene. From the relative location and local morphology of these regions, conclusions about possible routes for

TABLE VII Oxygen Index (OI) of films of PVA and PVA-clays nanocomposites (Film thickness equal 1.5 mm)

Composition	*OI, vol.%*
PVA	22.7
PVA + 10 wt.% kaolinite	24.5
PVA + intercalated montmorillonite	
4 wt.%	22.7
10 wt.%	23.7

hybrid formation can be deduced. Since the silicate layers are impenetrable in the direction perpendicular to their long axis, polystyrene must intercalate the gallery from the edges of the crystallites. For polymer to reach the crystallite edges, the melt must first penetrate the primary particles. Thus on the scale of the primary particle, two pathways are possible for polymer transport into the primary particle. Either polymer intercalation takes place uniformly throughout the primary particle or as a front penetrating the primary particle from the exterior. If hybrid formation occurred uniformly throughout the primary particle, the distribution of intercalated and unintercalated regions within the primary particle should be uniform and a substantial number of crystallites should contain both intercalated and unintercalated regions. However the predominance of intercalated crystallites at the exterior of the primary particle and the absence of crystallites containing both intercalated and unintercalated regions imply the second mechanism is more likely in polystyrene intercalation.

In the work [10] authors synthesized the polypropylene-clay hybrid. The silicate layers of clay mineral have polar hydroxyl groups and are incompatible with polyolefine. Therefore the clay gallery modified with nonpolar organic molecules. Organophylic clay was obtained by a cation-exchange reaction between Na-montmorillonite and the distearyl-dimethylammonium ion, and its inorganic content was 52.8 wt.%. A polypropylene oligomer with telechelic OH groups was dissolved in toluene, and equal quantities of organophylic montmorillonite was added to the solution. Then toluene was evaporated. Polypropylene diol was intercalated into the clay gallery, and its inorganic content was 24.7 wt.%. This polypropylene diol-clay nanocomposites or Na-montmorillonite and homopolypropylene were mixed using a Labo-Plastomill at 220°C until the motor torque became constant (about 5 min). Homopolypropylene was mixed with the organophylic or Na-montmorillonite. The inorganic (clay) content of these composites was 5 wt.%. To confirm the dispersion of clays in polypropylene a TEM observation was done for the intersection of injection-molded samples by a Jeol-200CXTEM using an acceleration voltage of 200 kV. This investigation confirm good chemical affinity of polyolefine and the distearyldimethylammonium-montmorillonite so that polyolefine could be inserted into the clay gallery in the presence of toluene. After the toluene was evaporated the telechelic OH groups interact with the silicate layer through hydrogen bonding. Polyolefine oligomer with telechelic OH remained in the clay gallery and silicates of clay were exfoliated.

A polymer electrolyte melt intercalation of poly(ethylene oxide) (PEO) in mica-type silicates was reported in the work [32]. PEO and Na-montmorillonite were thoroughly mixed in an agate mortar, formed into a pellet using a hydraulic press and a pressure of 70 MPa, and heated at 80°C in ambient atmosphere for 0, 2 and 6 hours. Figure 8 shows the X-ray diffraction pattern of PEO/Na-montmorillonite hybrid before heating and after two and six hours at 80°C

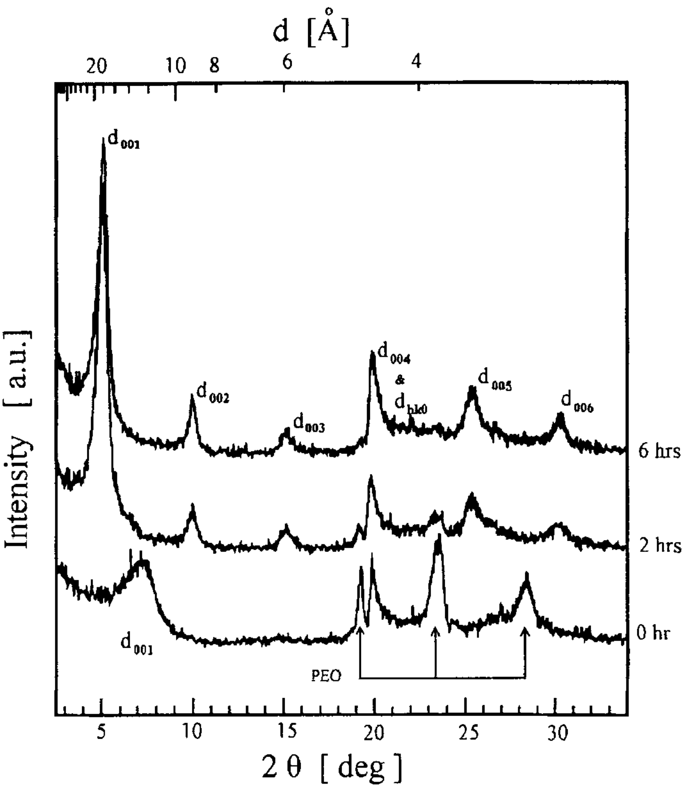


FIGURE 8 X-ray diffraction pattern of PEO/Na$^+$–montmorillonite hybrid heated to 80°C for 0, 2 and 6 hours.

respectively. After heating to 80° C the intensity of the peaks corresponding to the unintercalated silicate ($d = 11.4\,Å$) and crystalline PEO (4.6, 3.8 and 3.2 Å) is progressively reduced while a set of new peaks appears corresponding to the PEO-intercalated silicate (for example $d = 17.7\,Å$). After six hours only reflections corresponding to the PEO-intercalated silicate are observed signifying the completion of intercalation.

Differential scanning calorimetry (DSC) studies offer further evidence for intercalation. Figure 9 compares the DSC traces of PEO/Na-montmorillonite after 0, 2 and 6 hours at 80°C. Both the 0 and 2 hour traces clearly show a distinct endothermic corresponding to the melting transition of crystalline PEO. As the intercalation reaction progress, more PEO chains are intercalated and the area of the endothermic corresponding to the crystalline PEO is reduced. After six hours the transition has largely vanished suggesting that all the PEO is intercalated-consistent with the X-ray diffraction data that shows only reflections corresponding to the PEO intercalated phase.

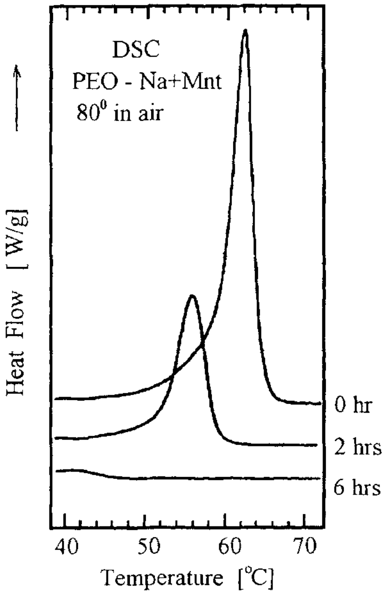


FIGURE 9 DSC traces for PEO/Na^+-montmorillonite hybrids heated to 80°C for 0, 2 and 6 hours.

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