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Review
Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites

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This paper focuses on polymer nanocomposites and their syntheses, properties and future applications, several of these application will be successful in the near future. This new type of materials, based on smectite clays usually rendered hydrophobic through ionic exchange of the sodium interlayer cation with an onium cation, may be prepared via various synthetic routes comprising exfoliation adsorption, *in-situ* intercalative polymerization and melt intercalation. The whole range of polymer matrices covered, i.e., thermoplastics, thermosets and elastomers. Small addition—typically less than 6 wt%—of these nanoscale inorganic fillers promote concurrently several properties of the polymer materials, including tensile characteristics, heat distortion temperature, scratch resistance, gas permeability resistance, and flame retardancy.

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1. Introduction
In recent years, organic-inorganic nanometer composites have attracted great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from two components. One of the most promising composites systems would be hybrids based on organic polymers and inorganic clay minerals consisting of layered structure, which belong to the general family of 2:1 layered silicates [1]. There is a great interest in polymer-clay nanocomposites. The dimension and microstructure of the dispersed phase significantly influence the properties of polymer composites. Polymer-clay nanocomposites have at least one ultra-fine dimension typically on the order of 1 to 10 nm. Because of the nanoscale structure, polymer-clay nanocomposites possess unique properties. As reported in the literatures, polymer-clay nanocomposites have improved mechanical and thermal properties [2–5], gas permeability resistance [6, 7] and fire retardancy [8].

This concept was first introduced by researchers from Toyota [9] who discovered the possibility to build a nanocomposite from polyamide 6 and an organophilic clay. Their new material showed dramatic improvements in mechanical and physical properties. Numerous other researchers later used this concept for nanocomposites based on epoxies [6, 10, 11], unsaturated polyester [12], poly (1-caprolactone) [13], poly (ethylene oxide) [14], silicone rubber [15, 16], polystyrene [17], polyimide [18], polypropylene [19], poly (ethylene terephthalate) [20], and polyurethane [21].

Nanocomposites can be produced by an *in-situ* polymerization or by melt/solution blending. The particular blending process which is used, as well as the time of annealing after the nanocomposite has been formed, have a significant influence on the structure, and hence the properties of the nanocomposite. When registry between the layers is maintained, the material is described as an intercalated material. When this registry is lost, and the clay layers are more randomly distributed throughout the polymer matrix, the system is described as an exfoliated or delaminated nanocomposite. Of course, if the clay is not dispersed, it is a simply filler and a nanocomposite is not formed [22]. Polymer composite materials are used widely in diverse applications such as transportation vehicles, construction materials, electronics and sporting goods and consumer products [23].

1.1. Structure of layered silicates
The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica

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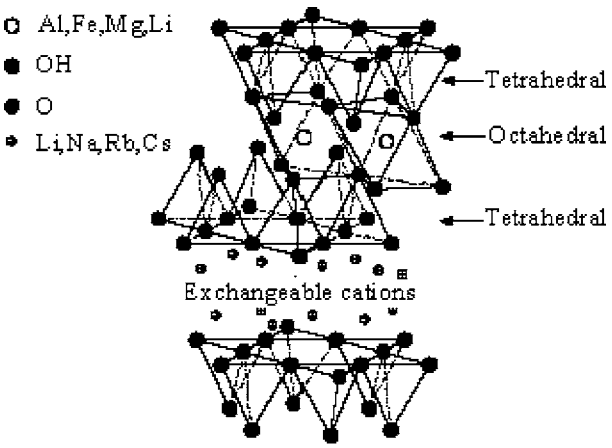


Figure 1 The structure of 2:1 layered silicates (adapted from [25]).

tetrahedron by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 Å to several microns and even larger depending on the particular silicate. These layers organize themselves to form stacks with a regular Van der Waals gap in between them called the interlayer or the gallery.

Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or by Fe^{2+}, or Mg^{2+} replaced by Li^{+}) generates negative charges that are counterbalanced by alkali or alkaline earth cations situated in the interlayer.

As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy [24]. In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations of the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium (onium). The modified clay (or organoclay) being organophilic, its surface energy is lowered and is more compatible with organic polymers. These polymers may be able to intercalate within the galleries, under well-defined experimental conditions, Montmorillonite, hectorite and saponite are the most commonly used layered silicates. Their structure is given in Fig. 1 [25] and their chemical formula are shown in Table I. This type of clay is characterized by a moderate negative surface charge (known as the cation exchange capacity, CEC and expressed in meq/100 g). The charge of the layer is not locally constant as it varies from layer to layer and must rather be considered as an average value over the whole crystal.

Proportionally, even if a small part of the charge balancing cations is located on the external crystallite surface, the majority of these exchangeable cations is located inside the galleries. When the hydrated cations are ion-exchanged with organic cations such as more bulky alkyammoniums, it usually results in a larger interlayer spacing.

TABLE I Structure and chemistry of Mica type layered silicates

Silicate	Location of isomorphous substitution	Formula
Montmorillonte	Octahedral	$M_x[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$[a]
Hectorite	Octahedral	$M_x[Mg_{6-x}Li_x](Si_8)O_{20}(OH)_4$
Saponite	Tetrahedral	$M_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$

[a] M = monovalent cation; x = degree of isomorphous substitution (between 0.5 and 1.3).

1.2. The structure of nanocomposites

The structure of the polymer-layered silicate nanocomposites has traditionally been elucidated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Due to the periodic arrangement of the silicate layers both in the pristine and the intercalated states, with periodicity of 1–4 nm and the presence of high atomic number species in the layers, the choice of X-ray diffraction in determining the interlayer spacing is obvious. However, in the absence of registry, as in an exfoliated or a delaminated nanocomposite, as well as in a disordered nanocomposite, XRD does not provide definite information regarding the structure of the nanocomposite e.g., polyethylene/C18FH nanocomposite and siloxane/C18FH delaminated hybrid (fluorohectorite modified with octadecylammonium cation is termed C18FH) (Fig. 2). In order to provide quantitative information in XRD 'silent' nanocomposites, TEM has proven to be an extremely useful technique. In addition to a description of the spatial correlations of the layered silicates, TEM also provides a means to discern the homogeneity of the mixing process.

A bright field TEM image of an organically modified layered silicate intercalated with polystyrene is shown in (Fig. 3a) The periodic alternating dark and light bands represent the layers of silicate and the interlayers respectively, with a spacing of ∼3 nm between the silicate layers. TEM also reveals the presence of individual crystallites consisting of several tens

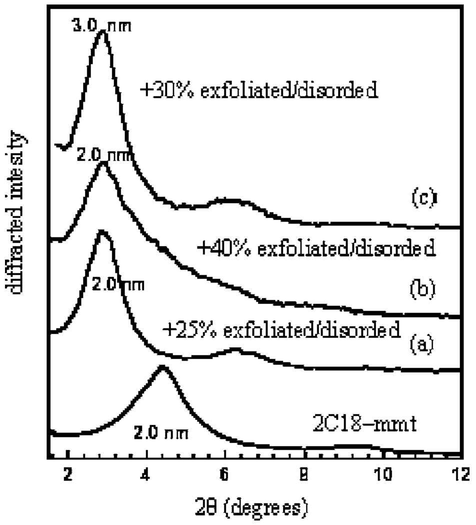
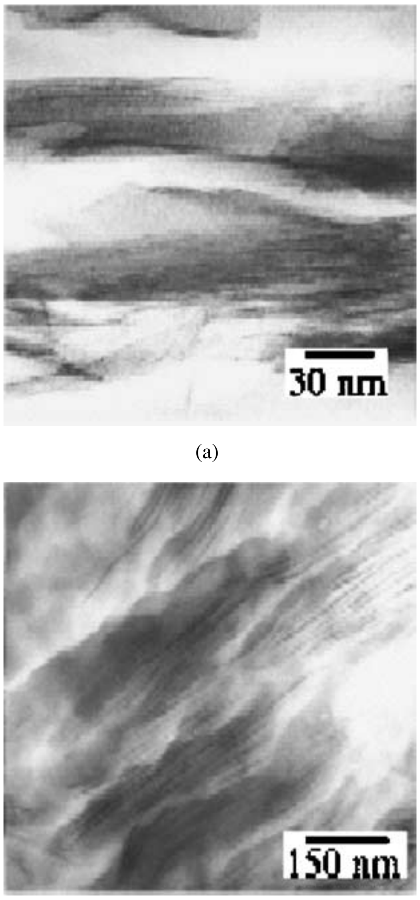


Figure 2 Typical XRD patterns from polymer/silicate hybrids: (a) XRD obtained from an "immiscible" system (here polyethylene/C18FH), and is identical with the XRD of the neat organosilicate (C18FH). For intercalated hybrids the d-spacing shifts to a higher value, (b) as the gallery expands to accommodate the intercalating polymer (here polystyrene/C18FH); second and third order reflections—as shown here—are very common and some times intercalated hybrids can have up to 13 order reflections [26], manifesting a remarkable long range registry and (c) Typical XRD of an exfoliated/delaminated structure or a disordered system (here a siloxane/C18FH delaminated hybrid).



(a)

(b)

Figure 3 TEM images of an intercalated (a) and an exfoliated and (b) hybrid [5].

of such silicate layers, with bulk polymer filling the space between the crystallites.

The pristine organically modified layered silicate exhibits the same microstructure as that observed in (Fig. 3a), with the exception of a smaller interlayer spacing. A TEM of an exfoliated hybrid of an organically modified layered silicate dispersed in epoxy is shown in (Fig. 3b). Such a hybrid, while being XRD silent, does in fact exhibit some relative layer order with spacing of a few tens of nm between layers. This is attributed to the intrinsic an isotropic dimensions of the layers with the aspect ratios of the individual layers being in the range of 100–1000. In addition, flexibility of the nanometer thick silicate layers is evident in this micrograph. Similar micrographs have also been obtained by Lan and coworkers [27] and the Toyota group using monomer intercalation followed by polymerization. Micrographs along with small angle X-ray scattering studies of oriented nanocomposites by the Toyota group [28–32] clearly demonstrate the difference observed in short length scale correlations in unaligned exfoliated nanocomposites (as present in Fig. 3b) and the long range correlations that are observed in aligned (using external shear and elongational flows) nanocomposites.

Recently, several attempts have been made to understand the underlying structural aspects of the silicate layers as well as the conformations of polymers in layered silicate based nanocomposites, using techniques such as small angle neutron scattering (SANS) and dynamic light scattering. Jinnai and coworkers [33] have studied mixtures of an organically modified vermiculite (modified with n-butylammonium) with poly (vinyl methyl ether) in the presence of n-butylammonium chloride and heavy water, using neutron scattering in order to elucidate the degree of chain interpenetration trapped in lamellar systems. They concluded that the introduction of polymer causes the silicate layers to become more strongly aligned with more regular, but generally decreasing interlayer spacing in the gel phase. On the other hand, the addition of polymer had no effect on the phase transition temperature between the tactoid and gel phases of the layered silicate. However, the conformation and location of the polymer chains in these mixtures were not unequivocally determined. Carrado *et al.* [34] have recently used SANS to monitor the effect of the change in the structure of the layered silicate (synthetic hectorites) upon hydrothermal crystallization with direct incorporation of poly (vinyl alcohol) (PVA). The results of these experiments established that the PVA appears to coat the small initially formed silicate particles, hindering their further growth. However, upon removal of the polymer no change has been observed in the extended inorganic network. Muzny and coworkers [35] have applied dynamic light scattering to monitor the dispersion of layered silicates in a polymer matrix. Specifically the dispersion of synthetic hectorite clay platelets suitably organically modified in a matrix of polyacrylamide was studied. These studies have clearly shown that a homogeneous (‘single layer dispersion’) was achievable only when a large excess (equivalent to five times the CEC of the silicate or higher) of the organic cationic surfactant was used.

2. Nanocomposite preparation

There are essentially three different approaches to synthesize polymer-clay nanocomposites: melt intercalation, solution and *in-situ* polymerization (as shown in Fig. 4).

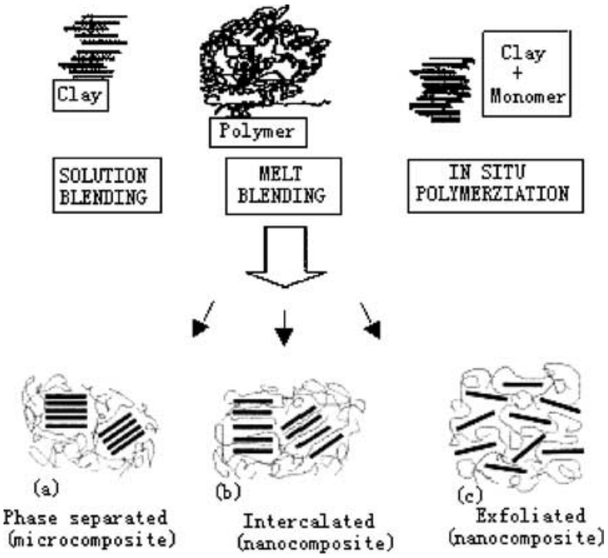


Figure 4 Schematic representation of various methods (solution blending, melt blending, and *in situ* polymerization) used to prepare polymer-layered-silicate nanocomposites.

2.1. Melt intercalation

This process was invented relatively recently by Vaia *et al.* [17]. A thermoplastic polymer is mechanically mixed with an organophilic clay at elevated temperatures. The polymer chains are then intercalated between the individual silicate layers of the clay. The proposed driving force of this mechanism is the enthalpic contribution of the polymer/organoclay interactions. This method is becoming increasingly popular since the resulting thermoplastic nanocomposites may be processed by conventional methods such as extrusion and injection molding.

2.2. Solution method

In the solution method, the organoclay, as well as the polymer, are dissolved in a polar organic solvent [30]. The entropy gained by the desorption of solvent molecules allows the polymer chains to diffuse between the clay layers, compensating for their decrease in conformational entropy [37]. After evaporation of the solvent, an intercalated nanocomposite results. This strategy can be used to synthesize epoxy-clay nanocomposites [38] but the large amount of solvent required is a major disadvantage.

2.3. *In situ* polymerization

The *in situ* polymerisation approach was the first strategy used to synthesize polymer-clay nanocomposites [27]. It is similar to the solution method except that the role of the solvent is replaced by a polar monomer solution. Once the organoclay has been swollen in the monomer, the curing agent is added and complete exfoliation occurs in favourable cases. According to the previous studies [39], the polymerization is believed to be the indirect driving force of the exfoliation. The clay, due to its high surface energy, attracts polar monomer molecules in the clay galleries until equilibrium is reached. The polymerisation reactions occurring between the layers lower the polarity of the intercalated molecules and displace the equilibrium. This allows new polar species to diffuse between the layers and progressively exfoliate the clay. Therefore, the nature of the curing agent as well as the curing conditions is expected to play a role in the exfoliation process.

3. Properties

Polymer-layered-silicate nanocomposites have unique properties when compared to conventional filled polymers [40]. For example, the mechanical properties of a Nylon-6-layered-silicate nanocomposite, with a silicate mass fraction of only 5%, show excellent improvement over those for pure Nylon-6. The nanocomposite exhibits increases of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength, and 126% in flexural modulus. The heat distortion temperature (HDT) is also increased, from 65 to 152°C, and the impact strengths are lowered by just 10% [4]. The mechanical properties of aliphatic amine cured epoxy-layered-silicate nanocomposites, reported recently by Wang and Pinnavaia, reveal an improvement of 400% or more in tensile modulus and tensile strength and a substantial increase in the strain-at-break [11]. Decreased gas permeability and increased solvent resistance also accompany the improved physical properties [41]. Finally, polymer-layered-silicate nanocomposites often exhibit increased thermal stability [15, 42] and, as will be discussed below, reduced flammability [43–48].

3.1. Thermal stability

Blumstein first reported the improved thermal stability of a polymer-layered-silicate nanocomposite that combined poly(methyl methacrylate) (PMMA) and montmorillonite clay [49]. Although this clay-rich nanocomposite (mass fraction $\geq$10% intercalated PMMA) undoubtedly exhibits mechanical properties dominated by the inorganic phase, the indication of enhanced polymer thermal properties are clear. Blumstein showed that PMMA inserted (d spacing increase of 0.76 nm) between the lamellae of montmorillonite clay resisted thermal degradation under conditions that would otherwise completely degrade pure PMMA (refluxing decane, 215°C, N^2, 48 h). These PMMA nanocomposites were prepared by free radical polymerization of methyl methacrylate (MMA) intercalated in the clay. Thermogravimetric analysis (TGA) reveals that both linear PMMA and cross-linked PMMA intercalated into Na^+ montmorillonite have a 40–50°C higher decomposition temperature. Blumstein argues that the stability of the PMMA nanocomposite is due not only to its different structure but also to restricted thermal motion of the PMMA molecules in the gallery.

3.2. Barrier properties

Generally, polymer/silicate nanocornposites are characterized by dramatic reductions in gas & liquid permeabilities, and at the same time, the solvent uptake decreases accordingly. Some comparative water vapor permeabilities are shown in (Fig. 5). Polymers ranging from epoxies and good sealants (such as siloxanes

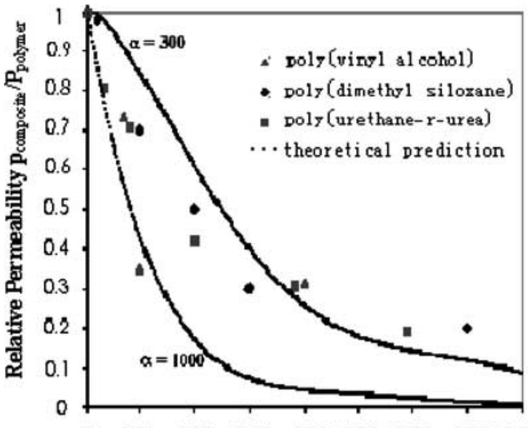


Figure 5 Water vapor permeability through polymer/MMt nanocomposites: poly (vinyl alcohol) [50], poly (urethane-urea) [51], and PDMS ‘nano’composites [52].

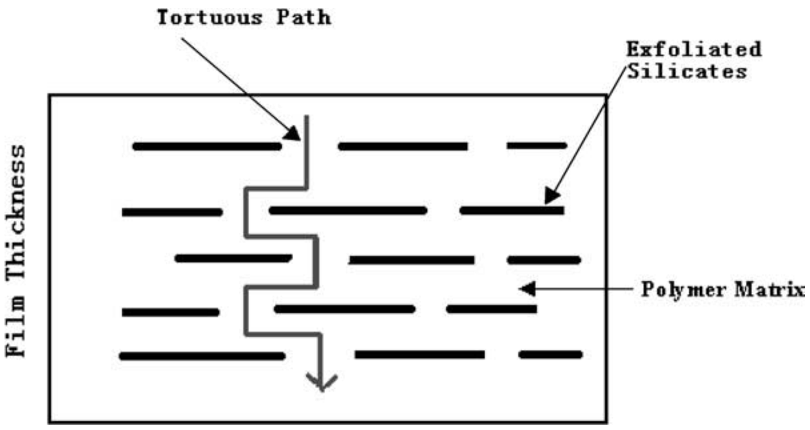


Figure 6 Illustration of Neilson's tortuous path model for barrier enhancement of nanocomposites.

[53–55]) to semi-permeable poly (urethane-urea) [51], to very hydrophilic PVA [50], are all improved up to an order of magnitude, for 5–7 wt% MMT loadings. This improvement can be attributed to the path tortuosity (Fig. 6); as well as the higher modulus promoted by the inorganic fillers, and thus, are strongly dependent on the hybrid structure (Fig. 5).

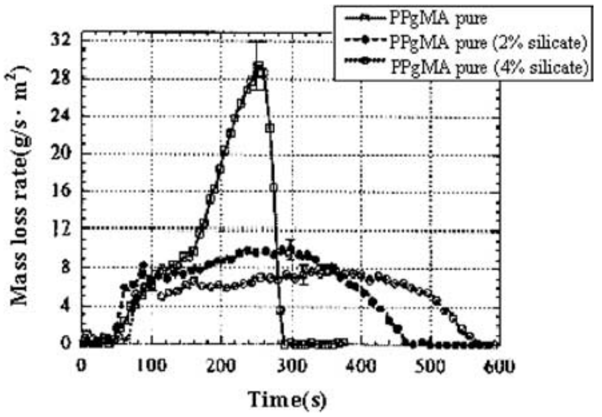


Figure 7 Mass loss rate from combustion of PP-MA/MMt hybrids (cone calorimetry study, from [60]). This is a general enhancement for a wide range of polymers [60].

3.3. Flame retardancy

The first mention of the potential flame retardant properties of these types of materials appears in a 1976 Unitika patent application on Nylon-6 layered-silicate (montmorillonite) nanocomposites [56]. However, not until more recent studies did the serious evaluation of the flammability properties of these materials begin [40]. Improvement in thermal stability similar to that reported by Blumstein for both poly(dimethylsiloxane) (PDMS) and polyimide nanocomposites has also been observed. In the case of PDMS, the nanocomposite was not prepared by *in situ* polymerization in sodium montmorillonite but by melt intercalation of silanolterminated PDMS into dimethyl ditallow ammoniumtreated montmorillonite [15]. In contrast to Blumstein's materials, this nanocomposite contained primarily PDMS (mass fraction 90%) and only a 10% mass fraction of montmorillonite. Despite the low clay content, the disordered-delaminated nano-structure shows an increase of 140°C in decomposition temperature compared to the decomposition temperature of the pure PDMS elastomer. In view of the barrier properties observed for other polymer nanocomposites, this increased thermal stability was attributed to hindered diffusion of volatile decomposition products within the nanocomposite. The TGA data for several aliphatic polyimide-layered-silicate nanocomposites also shows improved thermal stability as manifested in higher decomposition temperatures. Selfextinguishing flammability behavior was reported while burning the aliphatic polyimide-layered-silicate nanocomposites [42] and polycaprolactone nanocomposite [40]. Recent work done by Gilman *et al.*, using Cone calorimetry and radioactive gasification experiments, has also shown the improved flammability behavior of a number of other polymer-layered-silicate nanocomposites [43, 45, 57–59]. Montmorillonite-based fillers also promote the flame retardancy of polymers (Fig. 7), across a wide range of different chemistries [60]. Cone calorimetry studies by Gilman *et al.*, showed dramatic enhancements to polymers like PP, PS, nylon-6 and epoxies. This flame retardant character is traced to the response of a carbonaceous-char layer, which develops on the outer surface during Combustion [60].

This surface-char has a high concentration of MMt layers and becomes an excellent insulator and a mass transport barrier (slowing the oxygen supply as well as the escape of the combustion products generated during decomposition) [60].

3.4. Optical clarity

Clays are just into thin, albeit their micro- lateral size. Thus, when single layers are dispersed in a polymer matrix the resulting nanocomposite is optically clear in the visible region (Fig. 8). At the same time, there is a loss of intensity in the UV region (for $\lambda < 300$ nm), mostly due to scattering by the MMt particles. There is no marked decrease in the clarity due to nano-dispersed fillers compared to that of the neat-unfilled-polymer (for any relevant o-MMt loadings $\phi \leq 9$ wt%). This is a general behavior as seen by UV/vis transmittance for thick films (3–5 mm) of polymer/MMt nanocomposites, based on PVA [50], PP [61], and several epoxies.

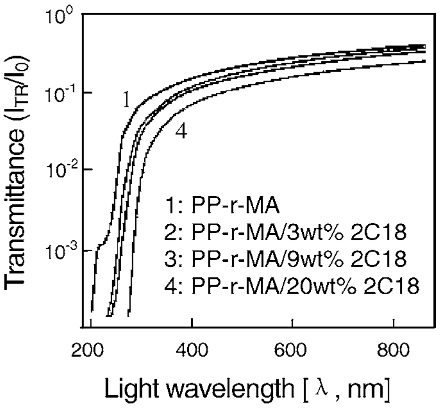


Figure 8 UV-vis transmittance for MA—functionalized PP and its MMt nanocomposites as a (unction of MMt loading ($\phi_{0-\mathrm{MMt}}$). From [61].

4. Applications

The nanocomposites have already been used widely in the various fields of injection molding, e.g., engine cover, timing belt cover, oil reservoir tank; and fuel hose in automobile industries, floor adjuster and handrail in the construction fields and various connectors in the electrical fields. Nanocompsite nylon6-clay hybrid (NCH) shows a high modulus and high distortion temperature [62]. The timing belt covers made from NCH by injection molding was the first example of industrialized use of polymer-clay nanocomposites. NCH has also a high gas barrier property because of the nanometer level dispersion of silicate layers [63], so it has a wide range of applications in the food packaging films. As mentioned above, the increased mechanical properties and dimension stability makes the nanocomposites convenient to be used as high value construction materials. They are highly stable against aggressive chemicals, so they can also be implemented in corrosive protective coatings.

Due to the decreased permeability for gases and water, as well as for hydrocarbons, they have a wide range of applications in packaging and automotive industries. In high temperature areas, such as internal combustion engines, because of good thermal stability, flame retardancy and HDT; nanocomposites are more attractive and promising than other conventional materials.

These materials have a good perspective of application for the near future in daily life. Through the nano-clay reinforcement we expect a new dimension in the polymer technology. The production of the high-tech composites like carbon-carbon composites is extremely expensive and labour-intensive, therefore the art of composites may be considered as another alternative solution. By the extrusion technology, lower labour-intensive mass production lines are expected.

5. Summary

Polymer/clay nanocomposites are materials that display rather unique properties, even at low clay content, by comparison with more conventional mineral-filled polymers. Nanocomposites have a number of advantages over traditional polymer composites. Conventional composites usually require a high content (>l0 wt%) of the inorganic filler to impart the desired mechanical properties. Such high filler levels increase the density of the product and can cause deterioration in properties through interfacial incompatibility between the filler and the organic matrix.

Processability also worsens as filler content increases. In contrast, nanocomposites show enhanced thermal and mechanical properties with even a small amount of added clay because the nanoscale dimensions of the clay particles yield a large contact area between the polymer and the filler. The structure of clays, with layers of high aspect ratio, also imparts excellent barrier properties, which in turn provides low gas permeability and enhanced chemical resistance and flame retardancy. This new type of materials, based on smectite clays usually rendered hydrophobic through ionic exchange of the sodium interlayer cation with an onium cation, may be prepared via various synthetic routes comprising exfoliation adsorption, *in situ* intercalative polymerization and melt intercalation. The whole range of polymer matrices is covered, i.e., thermoplastics, thermosets and elastomers.

Nanocomposites are subject of current interest because of their unusual magnetic, optical, electronic properties, which often different from their bulk properties. The reasons for these are confinement of electronic and vibrational excitation, quantum size effect and large surface to volume ratio. Although nanocomposites have received attention from both theoretical and experimental standpoints, the greatest challenge at present is to find out an effective synthesis procedure. The fundamental challenges in nanostructured materials are ability to control the scale (size) of the system, understand the influence of the size of building blocks in nanostructured materials as well as the influence of microstructure on the physical, chemical and mechanical properties of this material and transfer of developed technologies into industrial applications including the development of the industrial scale of synthesize methods of nanomaterials and nanostructured systems.

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