Origins of the Materials Properties Enhancements in Polymer/Clay Nanocomposites ‡

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Summary

Understanding the structure/property relations in polymer/clay nanocomposites is of great importance in designing materials with desired properties. Along these lines, a critical overview is attempted on the physical and molecular origins of material properties enhancements in polymer/clay hybrid nanocomposites. A comparative discussion of mechanical, thermal, optical, and flammability properties across various polymers focuses on those properties that are universally improved. In general, such properties originate from the nature of the layered inorganic fillers and from their nano-dispersion in a polymer. In contrast, other properties are determined by the particular/distinctive interactions between a specific polymer with the filler; such attributes can not be transfered from one polymer system to another. We shall try to distinguish between these two classes of properties, and provide some insight into which properties can be improved concurrently across a wide range of polymers.

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publications & references at: `http://zeus.plmsc.psu.edu/nano.html`

Introduction

The very large commercial importance of polymers has also been driving an intense investigation of polymeric composites reinforced by particulates, fibers, and layered inorganic fillers [1, 2]. In particular, in the case of layered inorganic fillers, talc and mica had been traditionally attracting the most interest. However, recent advances in polymer/clay and polymer/layered-silicate nanocomposite materials [3, 4] have aspired efforts to disperse clay-based fillers in almost any polymer available, usually expecting that complete exfoliation of the inorganic fillers in the polymer would yield the best performing systems.

Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays [5, 6], the field of polymer/clay nanocomposites has gained a large momentum recently. Two were the major findings that pioneered the revival of these materials: Firstly, the report of a nylon-6/montmorillonite material from Toyota research [**?**], where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Secondly, Giannelis *et al* found that it is possible to melt-mix polymers with clays without the use of organic solvents [7]. Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements of many materials properties by the nano-dispersion of inorganic layered fillers [8–11]. Where the property enhancements originate from the nanocomposite structure, these improvements are generally applicable across a wide range of polymers [4]. At the same time, there were also discovered property improvements in these nanoscale materials that could not be realized by conventional fillers, as for example a general flame retardant character [12] and a dramatic improvement in barrier properties [13, 14].

Although there exist many different natural and synthetic clays, dispersible in various polymers, in this paper we shall draw examples from polypropylene (PP) and montmorillonite (mmt) [15]. Montmorillonite is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge [5, 6]. The mmt crystal lattice consists of $1nm$ thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way, so that the oxygens from the octahedral sheet also belong to the silica tetrahedra). Isomorphic substitution within the layers (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}) generates a negative charge –defined through the *charge exchange capacity* (CEC)– and for mmt is typically 0.9-1.2 meq/g depending on the mineral origin. These layers organize themselves in a parallel fashion to form stacks with a regular van der Walls gap in between them, called *interlayer* or *gallery*. In their pristine form their excess negative charge is balanced by cations (Na^{+}, Li^{+}, Ca^{+2}) which exist hydrated in the interlayer. Obviously, in this pristine state mmt is only miscible with hydrophilic polymers, such as poly(ethylene-oxide) and poly(vinyl-alcohol) [13, 16]. In order to render mmt miscible with other polymers it is required to exchange the alkali counterions with cationic-organic surfactants, such as alkyl-ammoniums [3, 4].

Nanocomposite Formation & Structure

The thermodynamic challenge. In general, an interplay of entropic and enthalpic factors determines the outcome of whether an organically modified mmt (o-mmt) will be dispersed –intercalated or exfoliated– in a polymer [17–19]. Dispersion of mmt in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties [1]. Favorable enthalpy of mixing for the polymer/o-mmt is achieved when the polymer/mmt interactions are more favorable compared to the surfactant/mmt interactions [17–19]. For most polar or polarizable polymers, an alkyl-ammonium surfactant (the most commonly used organic modification) is adequate to offer sufficient *excess enthalpy* [2] and promote the nanocomposite formation.

General polymer/clay nanocomposite structure. Due to its easiness and its availability X-Ray Diffraction (XRD) is most commonly used to probe the nanocomposite structure. However, the XRD can only detect the periodically stacked mmt layers; disordered (bunched together but not parallely stacked) or exfoliated layers are not detected. In general, in natural-clay filled polymers with favorable thermodynamics for nanocomposite formation, the structure is characterized by a coexistence of exfoliated, intercalated and disordered layers. In figure 1 we show a bright-field TEM of a maleic anhydride functionalized polypropylene (PP-r-MA) nanocomposite, containing 6 wt% of 2C18-mmt. From the TEM it becomes clear that there are intercalated tactoids (A) and disordered/exfoliated stacks of layers (B) *coexisting* in the nanocomposite structure. Only the intercalated structures give rise to XRD reflections as those of figure 1, whereas the disordered mmt formations have no periodic stacking and thus remain XRD silent. This behavior is common for most polymer/mmt nanocomposites [3, 4], and typically the larger –in lateral size– mmt layers create intercalated tactoids, whereas the smaller layers tend to exfoliate[3]. The mixed exfoliated/intercalated structure is intrinsic in mmt-based nanocomposites and originates from the chemical and size inhomogeneities of the mmt layers. Only in very high lateral size ($>3\mu m$) layered fillers (such as vermicullites or synthetic fluorohectorites) there develops a *single* intercalated structure for all the tactoids [20].

To be on the safe side, XRD should be always accompanied by TEM investigations, since generally there is a coexistence of structures: thus, a silent XRD may hide a large number of disordered tactoids, whereas an XRD with an intercalated peak may not reveal extensive levels of exfoliation (fig. 1). In both cases, the nanocomposite properties can be *dramatically* affected by the structures that are not manifested in the XRD.

[1] confinement of the polymer inside the interlayers results in a decrease in the conformational entropy of the polymer chains. However, this entropic penalty of polymer confinement may be compensated in part by the increased conformational freedom of the tethered surfactant chains, that are located in a less confined environment as the layers separate [17–19]

[2] excess enthalpy in the sense of polymer/mmt interactions being more favorable than the alkyl-surfactant/mmt interactions

[3] this behavior should be very familiar to anyone that has ever calculated the surface forces necessary to separate two colloidal plates, such a force scales with the plate area

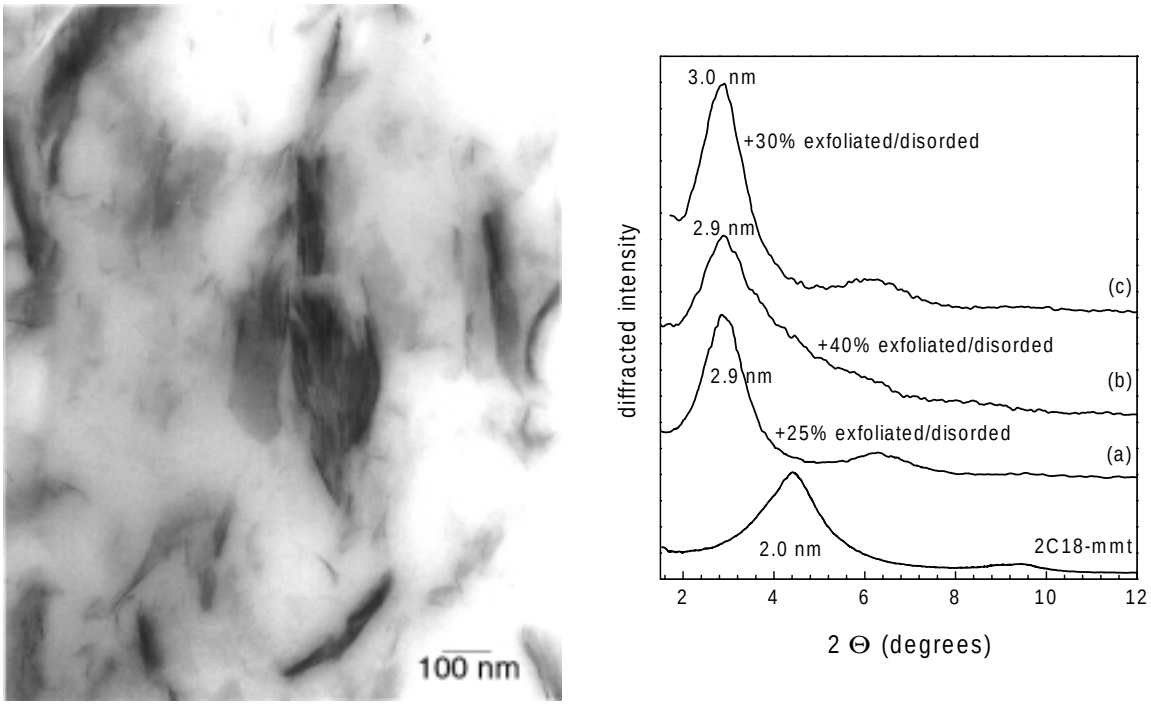


Figure 1: *Bright-field TEM (left) of a PP/mmt nanocomposite, where polypropylene has 0.5 mol% of maleic-anhydrite styrene comonomers. There is a coexistence of intercalated (A) and exfoliated or disordered (B) mmt structures. The corresponding XRD (right: b) shows a nice reflection at 2.9nm. PP/mmt nanocomposites with different functionalizations [1 mol% methylstyrene (a), and 0.5 mol% hydroxy-propyl-styrene (b)] show very similar XRD, albeit containing different levels of exfoliated layers. Figures from [15].*

If needed, quantitative analysis of TEM images can be used to evaluate the percentage of silicate exfoliation. For example, the numbers reported on fig. 1 were evaluated as follows: For each nanocomposite material we capture 20 to 40 independent TEM images at 50K magnification (a view of approx. $4\times5\mu m$). Subsequently, we use image analysis software to enumerate: (a) the total number of layers seen edge-on; (b) the layers in stacks of more than 10 layers separated by less than $3nm$ (tactoids); and (c) bunches of up to three layers that are separated by more than $50nm$ (exfoliated layers) or non-parallel layers separated by less than $20nm$ (disordered layers). The percentage of the last group is an estimation of the exfoliated and disordered structures in the system. Admittedly, these definitions are *ad-hoc* and 20-40 images cover too small an area to carry a high statistical significance, however, for the particular study they were sufficient to contrast the different PP/mmt nanocomposite structures [15].

Exfoliated structures by "trapping" layers apart. In many cases, polymer/clay systems that do not have favorable thermodynamics for nanocomposite formation, can be "trapped" in exfoliated structures (through solvent casting, or high shear-rate/high temperature extrusion). Such trapped structures are usually not thermodynamically stable nor

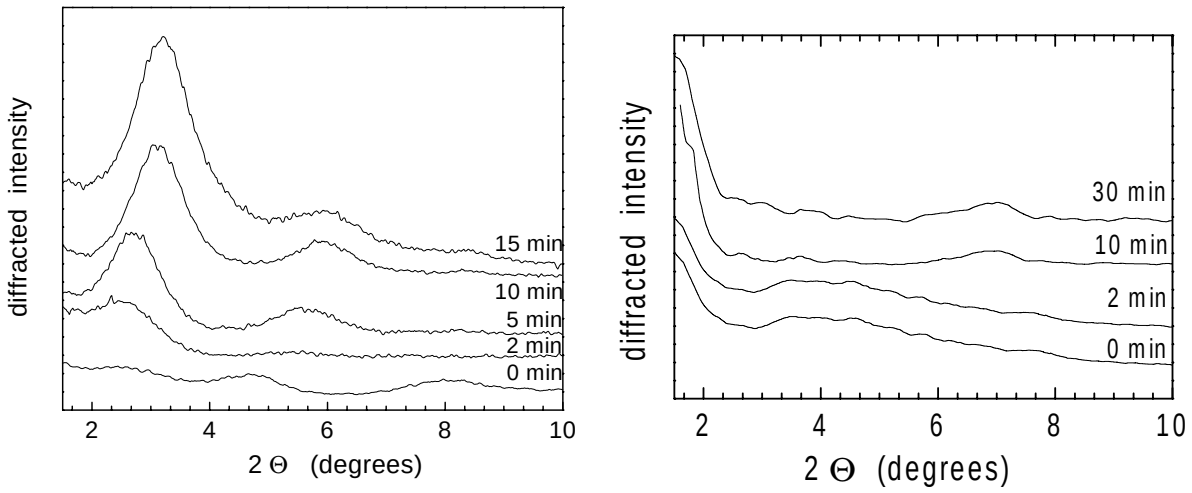


Figure 2: *The structure evolution/stability of neat-PP/2C18-mmt (left) and PP-MA/2C18-mmt (right) 'nano'composites, that were initially (0 min) trapped apart. XRD studies of compression molded samples are shown. For the neat-PP, 2C18-mmt very fast collapses to intercalated/immiscible tactoids, whereas for the MA-functionalized PP, the trapped exfoliated structure is maintained even under prolonged annealing. This suggests that the MA groups have sufficiently strong interactions with the mmt to prevent the polymer from sliding away from the inorganic layers.*

amiable to further processing. In fig. 2, we show the XRDs of precipitated PP/mmt hybrids from a co-suspension of polypropylene and o-mmt in trichloro-benzene (similar structures can be obtained from high $\dot{\gamma}$ extrusion [21–24]). Subsequently, we process these "hybrids" by compression molding (at 180°C/15 tons). This allows for the polymer to melt and the trapped hybrid structure to relax. If the o-mmt dispersion is not thermodynamically favored the layers will collapse in low d-spacing parallel stacks (e.g. neat-PP/dimethyl-dioctadecyl-ammonium-mmt fig. 2 left) during the high temperature processing, leading to a conventionally-filled 'macro'composite. However, if the there exists a favorable free energy of the o-mmt/polymer mixing, the exfoliated structure may be retained (e.g. PP-MA/dimethyl-dioctadecyl-ammonium-mmt fig. 2 right). This approach can yield stable dispersions only for polymers with strong specific interactions with mmt (e.g. polymers that hydrogen bond to the silicates, such as poly(vinyl alcohol) [13], poly(urethanes) [14], and nylon-6) it is striking that only 0.5 mol% of MA can have the same effect in PP.

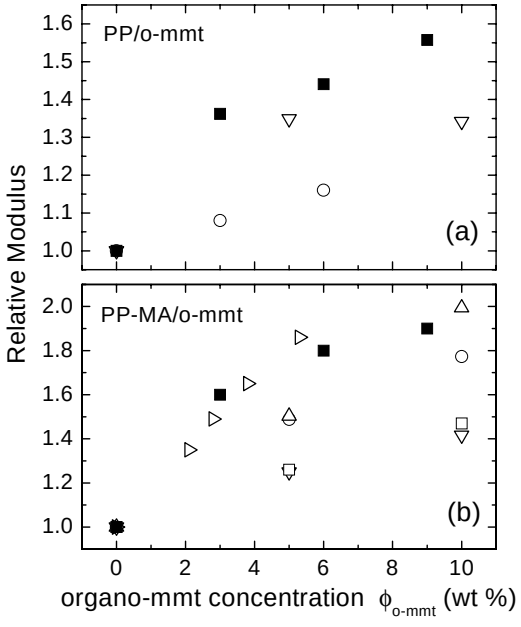
As expected, mechanical shear markedly reduces the time necessary for the structure relaxation, and the structure of figure 1(b) is recovered after 8 min of mixing (extrusion at 180°C). In concert, trapped systems of neat-PP/2C18-mmt even after very moderate mixing (1-3 min at 180°C) result in an immiscible/intercalated structure with a wide XRD reflection extending from 1.8 to 2.7nm in d-spacing.

At this point, we should note that this approach is qualitatively similar to the "swelling

agent" approach, as for example by Wolf et al. [25]. In such approaches an alkyl-ammonium-exchanged montmorillonite is intercalated by an organic "swelling agent", such as ethylene glycol, naphtha or heptane (all with boiling points below the processing/extrusion temperature) [25]. Subsequently, the swollen organo-modified clay is compounded with PP in a twin-screw extruder at 250°C. At this processing temperature, the swelling agent evaporates leading to the formation of a 'nano'composite which is XRD silent. In principle, this is the same as our solution intercalation experiment, where a solvent is employed to mix the o-mmt with the polymer, and an exfoliated structure is trapped when evaporating the solvent.

Materials Properties

Mechanical properties. Most of the polymer/clay nanocomposites studies report tensile properties, as a function of mmt content ($\phi_{\rm mmt}$), characterized by Instron. As a typical example, in fig. 3 we compare tensile moduli from various studies by Instron of neat-PP/o-mmt and MA-functionalized-PP/o-mmt nanocomposites, as well as respective "trapped" 'nano'composites. The characteristic behavior for polymer/layered-inorganic nanocomposite materials [4] is observed: Namely, there is a sharp increase of the Young's modulus for very small inorganic loadings ($\phi_{\rm o-mmt}$<4wt%) followed by a much slower increase beyond $\phi_{\rm o-mmt} \simeq$5wt%. With increasing $\phi_{\rm mmt}$, the yield stress does not change markedly compared



Heat Deflection Temperatures (HDT [26]) of PP/mmt nanocomposites and the respective unfilled (neat) PP. The f-mmt are mmt modified by semi-fluorinated alkyl surfactants [15]. From [15].

Organo-mmt filler loading $\phi_{\rm o-mmt}$ [wt. %]	HDT [°C] neat-PP/ f-mmt	HDT [°C] neat-PP/ alkyl-mmt
0 (neat PP)	109 ±3	109 ±3
3 wt.%	144 ±5	[a]130 ±7
6 wt.%	152 ±5	[b]141 ±7
9 wt.%	153 ±5	

[a] C18-mmt filler, by extruder
[b] 2C18-mmt filler, by twin-head mixer

Figure 3: *Tensile moduli (relative to bulk value) & HDT for various PP/mmt nanocomposites. (a) neat-PP hybrids: with f-mmt (■, [15]), C18-mmt (▽, [22]), and 2C18-mmt (◯, [15]). (b) PP-MA/2C18-mmt nanocomposite (■, [15]), and PP hybrids with various PP-MA pretreated o-mmt: C18-mmt (▷, [21]), C18-mmt (◯, △, [22]), and C8-mmt (▽, □, [22]).*

to the neat-polymer value, and there is a small only decrease in the maximum strain at break. PP systems conventionally filled –no nanometer level dispersion– by the similar fillers (e.g. 2C18-mmt) do not exhibit as large increases in their tensile modulus (figure 3a).

This mechanical reinforcement is expected and not too exciting at first glance. However, ther are some points that one can make:

- as the polymer/inorganic adhesion is improved –e.g. when MA functional groups are added to the polymer– the stresses are much more effectively transfered from the polymer matrix to the inorganic filler, and thus a higher increase in the Young's modulus is achieved (fig. 3b)
- the tensile results obtained from thermodynamically stable hybrids are not affected by processing conditions (since the nanocomposite structure remains the same) whereas, in absence of favorable PP/o-mmt thermodynamics, the structure and the tensile properties vary strongly with the processing conditions (fig. 3b)
- similar improvements in mechanical properties can also be achieved by other layered particulate fillers, however, much higher filler loadings are required (e.g. by loading 30-60 wt% of talc or mica [27])

Heat Deflection Temperature. If the mechanical reinforcement of PP due to the nanocomposite formation was limited only to the tensile modulus increase, this would have been an uninteresting system. The nano-dispersion of mmt in the PP matrix also promotes a higher heat deflection temperature (HDT [26]). In the case of neat-PP/f-mmt there is a marked increase of the HDT, from 109°C for the neat polymer to 152°C for a 6 wt.% nanocomposite. When the same neat-PP polymer is filled with alkyl-ammonium modified mmt the HDT is also increased but to a smaller extent, reflecting the lower exfoliation level of the inorganic fillers. Moreover, in the latter case, there is a strong dependance of the HDT on the processing conditions during the composite formation, similarly to the tensile properties. The increase of HDT due to mmt dispersion is a very important improvement for PP, not only from the application/industrial viewpoint, but also because it is difficult to achieve similar HDT enhancements by chemical modification or reinforcement by other fillers [27].

The improvement of the HDT originates from the better mechanical stability of the nanocomposite, compared to the neat-PP, rather than any increase of the polymer melting point. In all the PP/mmt hybrids studied, the melting temperature does not change markedly from that of the respective neat polymer. This is qualitatively different from the behavior of other polymers (e.g. nylon-6), where the mmt layers stabilize a different crystalline phase than found in the neat polymer, with higher melting point and also higher HDT [?].

Other properties

Beyond the mechanical and HDT improvements, the nanocomposite formation results in *concurrent enhancements* of other materials properties [4]. Since tensile properties can also be

improved by other means, the highest potential for any future applications of such nanocomposites do actually relate to these "other property" enhancements. In brief, we will discuss some examples that qualitatively set apart the polymer/clay nanocomposites from other conventional composites:

Barrier Properties. Generally, polymer/silicate nanocomposites are characterized by very strong reductions in *gas & liquid permeabilities*, and at the same time, the *solvent uptake* decreases accordingly. Polymers ranging from epoxies and good sealants (like siloxanes [9]), to semi-permeable poly(urethane-ureas) [14], to very hydrophilic PVA [13], are all improved up to an order of magnitude, for 5-7 wt% mmt loadings. This improvement can be attributed to the path tortuosity, as well as the higher modulus promoted by the inorganic fillers.

Flame retardancy. Montmorillonite-based fillers also promote the *flame retardancy* of polymers, across a wide range of different chemistries [12]. 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 [12]: 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) [12].

Optical Clarity. Albeit their micron lateral size, clays are just $1nm$ thin. Thus, when single layers are dispersed in a polymer matrix the resulting nanocomposite is *optically clear* in the visible region. Whereas, there is a loss of intensity in the UV region (for λ<$250nm$), mostly due to scattering by the mmt particles. There is no marked decrease in the clarity due to nano-dispersed fillers (for relevant [4] o-mmt loadings $\phi \leq$9 wt%). This is a general behavior

[4] one has to load 20 wt% of 2C18-mmt in $3mm$-thick film of PP before there develops haze observable by the bare-eye

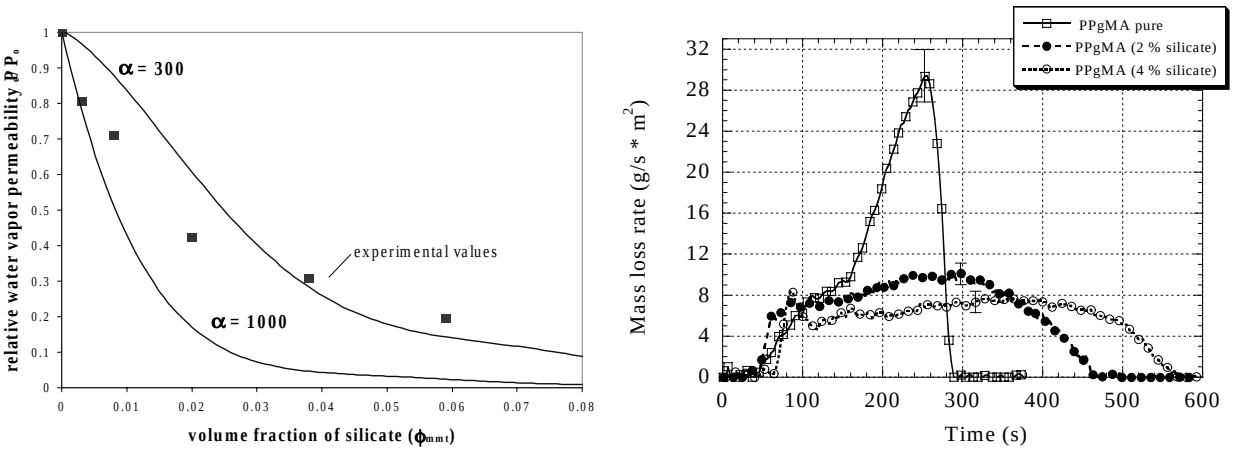


Figure 4: *Water vapor permeability through poly(urethane-urea)/mmt hybrids (from [14]). Mass loss rate from combustion of PP-MA/mmt hybrids (cone calorimetry study, from [12]).*

as seen by UV/vis transmittance for thick films (3-5mm) of polymer/mmt nanocomposites, based on PVA [13], PP [15], and several epoxies.

Processing and synergy with other fillers. Where there exist favorable thermodynamics for polymer/clay miscibility, the organo-clay can be incorporated in the final stages of polymer processing (e.g. extrusion, injection/compression molding) and obtain nanocomposite hybrids. Thus, polymer/mmt nanocomposites are amiable to most of the common processing techniques in today's industrial practices, which lowers the barriers towards commercialization for these nanocomposite hybrids. Additionally, o-mmt fillers can be used in conjunction with other reinforcements, such as fibers, thus combining the nanocomposite improvements and those from the fiber reinforcement in one composite material.

Conclusions

For polymer/organo-clay systems with favorable thermodynamics of mixing, nanocomposite formation can be achieved by melt-intercalation (unassisted by mechanical shear or solvents), extrusion, and compression/injection molding. The structure of these nanocomposites (nano-dispersion of fillers) does not change markedly with processing, since it is dictated by the thermodynamics. For naturally occurring fillers (such as mmt) there usually coexist exfoliated, disordered and intercalated layers.

Due to the nanocomposite structure, the hybrids exhibit concurrent improvements in several materials properties, for very moderate inorganic loadings (typically less that 6 wt% of mmt). Enhanced properties include improved tensile characteristics, higher heat deflection temperature, high barrier properties, and increased flame retardancy. At the same time, optical clarity and light weight are largely maintained. Since most polymer/clay nanocomposites are amiable to common processing techniques –and can be further reinforced by traditional fillers, such as fibers– these hybrid materials hold a high promise for pushing the envelope of usage for each polymer towards new potential applications.

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