Multifunctional Polymer/Inorganic Nanocomposites

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Abstract

The nanometer dispersion of inorganic ultra-thin layered fillers in polymers have been proven a very successful route to concurrently enhance several properties of the polymer matrix, and result in multifunctional nanocomposite materials. Understanding the structure/property relations in polymer/clay nanocomposites is of great importance in designing materials with desired sets of properties. Along these lines, a critical overview is attempted on the physical and molecular origins of material properties enhancements in polymer/inorganic hybrid nanocomposites, in the context of designing a multifunctional composite.

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 (mmt) material from Toyota research [7], 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 [8]. 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 [9, 10, 11, 12]. Where the property enhancements originate from the

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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[13] and a dramatic improvement in barrier properties [14, 15].

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 [16, 17, 18]. Dispersion of mmt in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties [2]. 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 [16, 17, 18]. For most polar or polarizable polymers, an alkyl-ammonium surfactant (the most commonly used organic modification) is adequate to offer sufficient *excess enthalpy* [3] and promote the nanocomposite formation.

Additional challenge for high-Temperature polymers. In many cases, although the thermodynamics of mixing between a specific polymer and organically modified silicates/clays are well known, and alkyl-ammonium based silicates are readily available commercially, the poor thermal stability of the ammonium group limits the ability to melt-process miscible nanocomposites. Examples of such cases include syndiotactic polystyrene (s-PS) and poly(ethylene terephthalate) (PET). Namely, numerous systematic studies [17, 19] of atactic polystyrene (PS) provide detailed information for the necessary organic modification for silicates (montmorillonite, hectorite, etc) so as to become miscible (intercalated/exfoliated) with styrene-based polymers. Along the same lines, it is also well-known how to modify silicates of varied CEC to render them miscible with esters and phenolics, thus, there exists an accurate guide on how to design silicate organic modifications for PET and s-PS. Imidazolium-alkyl organic modifications can be employed in such cases; despite the replacement of the ammonium by the more thermally stable aromatic cationic group, i.e. imidazolium, organic alkyl-tails at the appropriate size and hydrophobicity, will still maintain favorable thermodynamics for the dispersion and, while at the same time, imidazolium enables higher temperatures for melt-blending (e.g. processing temperature above *ca.*240°C, such as needed for s-PS (Tm = 270°C) or PET (Tm = 265°C).

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.

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[2] 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 [16, 17, 18]

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

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 [4, 3], and typically the larger –in lateral size– mmt layers create intercalated tactoids, whereas the smaller layers tend to exfoliate[4]. 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

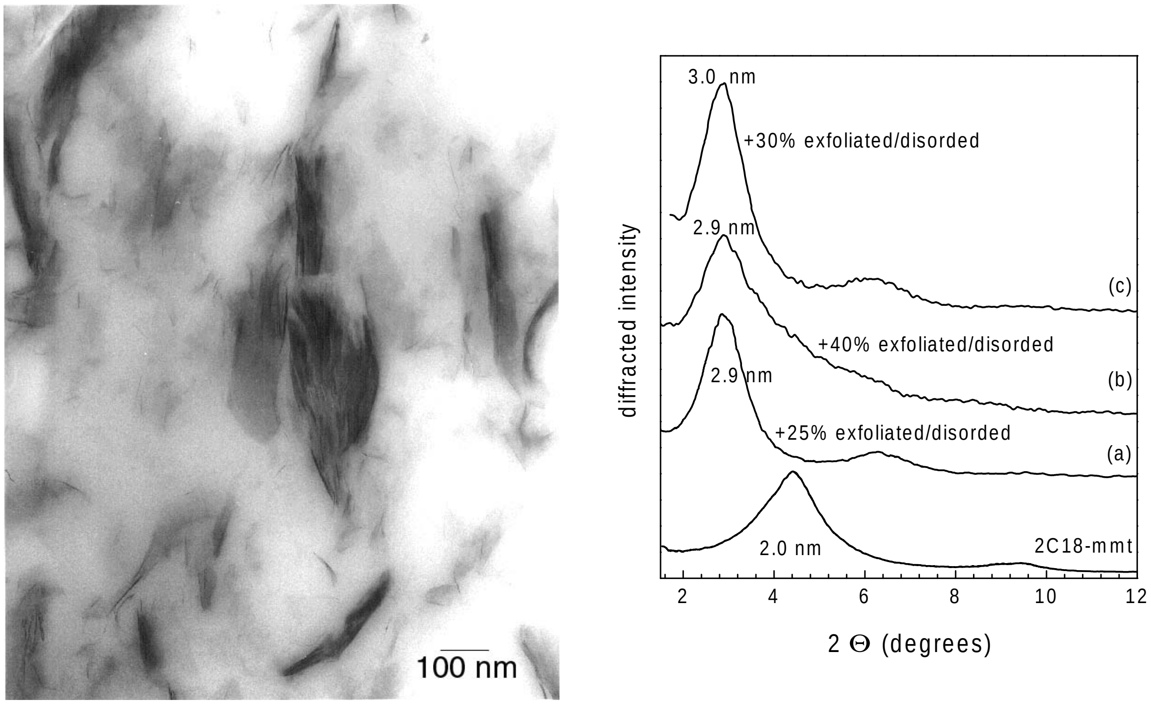

Figure 1: *Bright-field TEM (left) of a PP/mmt nanocomposite, where polypropylene has 0.5 mol% of maleic-anhydrite styrene comonomers. There is a coexistence of intercalated (A) and exfoliated or disordered (B) mmt structures. The corresponding XRD (right: b) shows a nice reflection at 2.9nm. PP/mmt 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 [20].*

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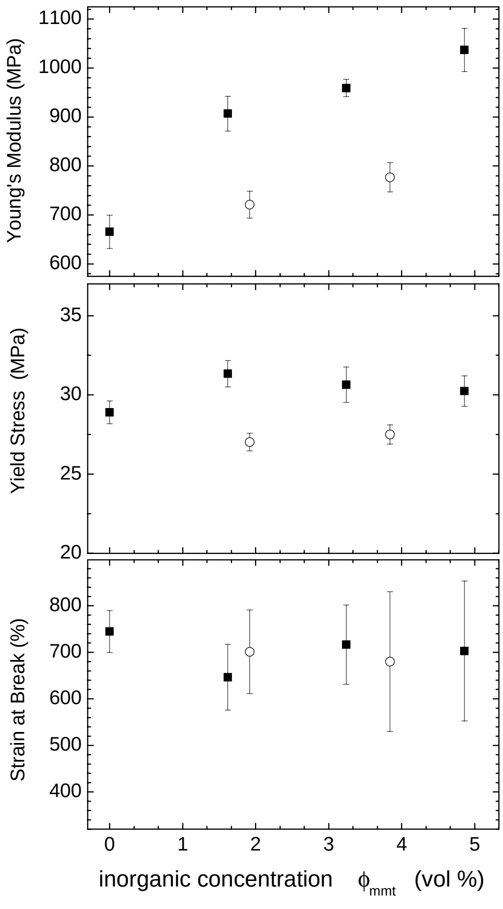
[4] this behavior should be very familiar to anyone that has ever calculated the surface forces necessary to separate two colloidal plates, such a force scales with the plate area

($>3\mu m$) layered fillers (such as vermicullites or synthetic fluorohectorites) there develops a *single* intercalated structure for all the tactoids [19].

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.

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. 2 we compare tensile properties by Instron of neat-PP and its respective mmt-based nanocomposites. 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 [21]) of PP/mmt nanocomposites and the respective unfilled (neat) PP. The f-mmt are mmt modified by semi-fluorinated alkyl surfactants. From [20].

Organo-mmt filler loading $\phi_{\rm o-mmt}$ [wt. %]	HDT [°C]	
	neat-PP/ f-mmt	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 2: *Tensile properties & HDT for PP/mmt nanocomposites (■, [20]), and conventional composites that contain mmt which is not well-dispersed in the PP matrix (□, [20]).*

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 2).

This mechanical reinforcement is expected and not too exciting at first glance. However, ther are some important points that should be emphasized:

- the traditional 'trade-offs' in property improvements can be overcomed, for example upon composite formation with traditional fillers any improvement is stiffness is accompanied by a decrease in strength; for nanocomposites this is not the case, since stiffness can be substantially improved without marked loss of strength (fig. 2)
- 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. 2, also [20, fig.8])
- 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 [22], compared to 2-3wtlayered nanoparticles)

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 [21]). 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 [22].

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 [7].

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 [10]), to semi-permeable poly(urethane-ureas) [15], to very hydrophilic PVA [14], 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 [13]. 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 [13]: 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) [13].

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 $\lambda < 250nm$), mostly due to scattering by the mmt particles. There is no marked decrease in the clarity due to nano-dispersed fillers (for relevant [5] o-mmt loadings $\phi \leq 9$ wt%). This is a general behavior as seen by UV/vis transmittance for thick films (3-5mm) of polymer/mmt nanocomposites, based on PVA[14], PP[20], and several epoxies.

Processing and synergy with other fillers. Where there exist favorable thermody-

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

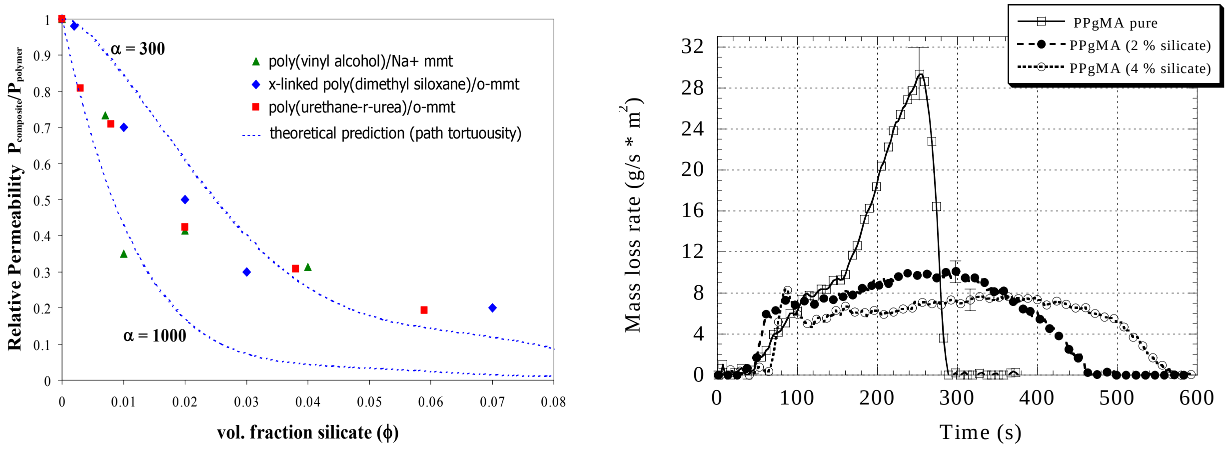

Figure 3: (left) *Water vapor permeability through various polymer/mmt hybrids, normalized by the unfilled polymer permeability.* (right) *Mass loss rate from combustion of PP-MA/mmt hybrids (cone calorimetry study, from [13]).*

namics 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/inorganic and polymer/clay systems that are designed to obey favorable thermodynamics of mixing, can lead to nanocomposites of a multi-functional character, i.e. with several materials properties concurrently improved. 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). Especially those materials properties that depend on the surface area of the fillers, and/or on the amount of physisorbed/bound polymer are particularly affected: Such properties include tensile characteristics, heat deflection temperature, barrier properties, and flame retardant character. 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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