The role of nanometer-thin layered inorganic fillers as flame retardants in polymers

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ABSTRACT

A critical view of the structure and properties of polymer/silicate hybrids is aimed to provide insights on how nanometer-thin, layered, inorganic fillers reduce the flammability of polymers. The flame retardant character of these composite materials is traced to a formation of a surface char upon combustion, and to the increased barrier and higher heat stability due to the fillers. A detailed discussion of the later materials properties offers some understanding on how general the increase of flame retardancy is across polymers, and whether it can be synergistic with other flame retardant additives.

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 inspired 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.

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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. 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 [7–9]. Where the property enhancements originate from the nanocomposite structure, these improvements are generally applicable across a wide range of polymers [4]. Examples include increased tensile modulus with no sacrifice of strength, elevated softening temperature (HDT) and decreased coefficient of thermal expansion, enhanced scratch resistance, while retaining the polymer's optical clarity in the visible wavelengths. At the same time, there are also additional property improvements in these nanoscale materials that can not be realized by conventional solid fillers, as for example a general flame retardant character [10–15] and a dramatic improvement in barrier properties [16,17].

The scope of this paper is to trace the origins of the flame retardant character in polymer/layered-silicate and polymer/clay nanocomposites, and the interconnection with other properties, namely the enhanced thermal stability and improved barrier properties. In this effort, we review our relevant work and also work by others, aiming to derive some generally applicable principles that dictate the behavior of these hybrid composite materials.

FLAMMABILITY OF POLYMER/LAYERED-SILICATE HYBRIDS

Among others J.W. Gillman and collaborators have systematically studied the flammability of polymer/layered-inorganic composites, with the emphasis on polymer/ montmorillonite and polymer/ fluorohectorite hybrids [10–14]. Several polymer systems have been investigated using cone calorimetry studies, including nylon-6 [12,14], bisphenol-based epoxies [12,13], vinyl-esters [13], polypropylene [10,13,14], and polystyrene [10,13,14]. In these studies, cone calorimetry was used to measure the heat release rate and other flammability properties of the nanocomposites, under well-controlled combustion conditions. Both the polymer-layered silicate nanocomposites and the combustion residues were studied by transmission electron microscopy and X-ray diffraction [10]. Evidence was found for a common mechanism of flammability reduction, and it was also found that the type of layered silicate, nanodispersion, and processing degradation have an influence on the flammability reduction.

Namely, layered silicate fillers (such as mmt and FH) promote flame retardancy in polymers, across a wide range of different chemistries [10]. Cone calorimetry studies by Gillman *et al*, showed parallel 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 [10]: 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) [10]. The nanocomposite structure (exfoliated, intercalated, or mixed) and the chemical details of the polymer and the surfactant have been found to affect the combustion behavior of these systems [10].

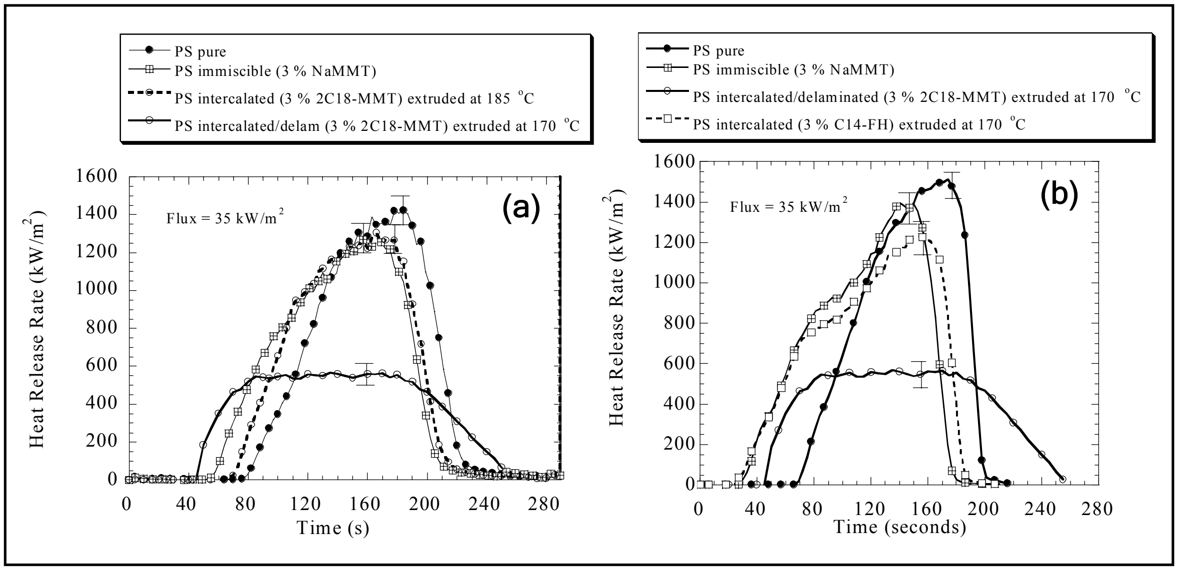

Figure 1: Cone calorimetry heat release rates of polystyrene (PS) nanocomposites with (a) natural montmorillonite, and (b) synthetic fluorohectorite, from [10]. The effect of nanocomposite structure on the flammability behavior of polymer/layered-silicate hybrids is demonstrated by keeping the inorganic filler the same [mmt in (a) and FH in (b)] and tuning the structure through careful choice of the alkyl-ammonium surfactant. For immiscible, intercalated, and conventionally filled composites –i.e. no nanometer filler dispersion– there is a small only change in HRR, whereas where nanometer delamination is achieved –exfoliated or partially exfoliated structures– there is a marked decrease of the maximum HRR compared to the pure polymer.

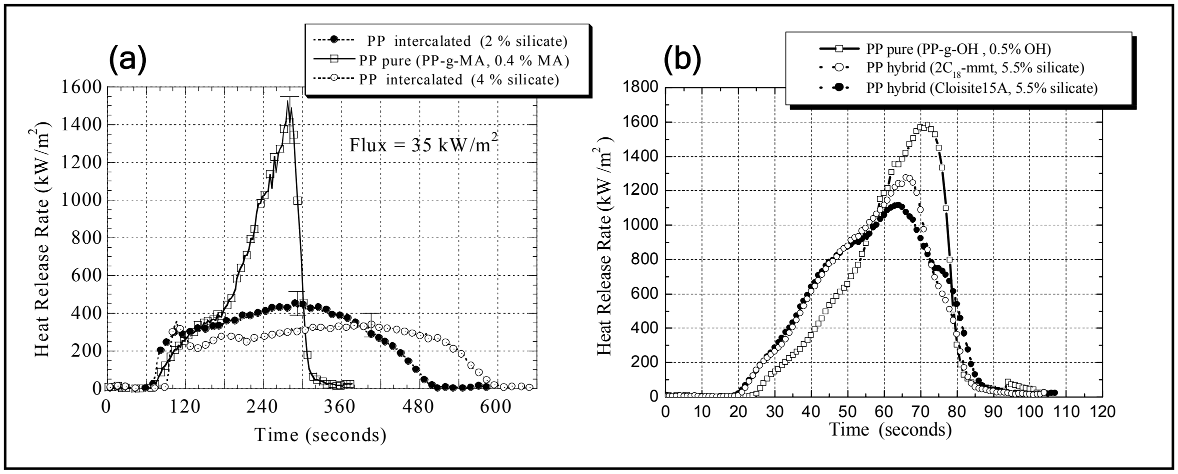

Figure 2: Cone calorimetry HRR of polypropylene (PP)/mmt nanocomposites. Two different functionalized PP are shown: (a) PP with 0.4% of maleic-anhydrite groups (from [10]), and (b) PP with 0.5% of hydroxyl containing groups [18]. Although in both cases fine dispersion of the mmt is achieved in a partially exfoliated structure, it is obvious that the existence of small amounts of OH groups in the PP polymer reduce the improvement in flammability.

Specifically, comparing the cone calorimetry study of polystyrene (PS) with various layered silicate fillers [such as montmorillonite (mmt) figure 1(a), and fluorohectorite (FH) figure 1(b)] has shown the fine –nanometer– delamination of these fillers is necessary to promote the creation of an "insulating" char in the surface of the composite and increase flame retardancy [10]. Where the same filler is used and its surface modification (surfactant) is varied (figure 1) a decrease in flammability takes place only for those structures that contain finely dispersed/exfoliated silicates, even in coexistence with intercalated structures: mixed –intercalated and exfoliated– as in the case of mmt figure 1(a). Purely intercalated dispersion as in the case of FH figure 1(b) do not improve markedly the flame retardancy in comparison with the pure PS.

However the nanocomposite structure alone is not adequate to predict/explain the flammability of these hybrids, as shown in figure 2. For example, in the case of polypropylene (PP) partial delamination of alkyl-ammonium modified mmt can be achieved by adding a very small amount (0.5 molar%) of polar groups to PP [18]. The selection of the functional group does not dramatically affect the nanocomposite structure –i.e. the mmt dispersion– [18], but it can have a marked effect on the flammability of the nanocomposite (figure 2). In figure 2(a) a maleic anhydrite functional group was added to the PP polymer leading to a strong reduction of the maximum heat release rate. In contrast when the same amount of styrene-*ortho*-butyl-alcohol functional group was added to PP to form nanocomposites of similar –partially delaminated– structure [18], the flammability reduction becomes much smaller [figure 2(b)].

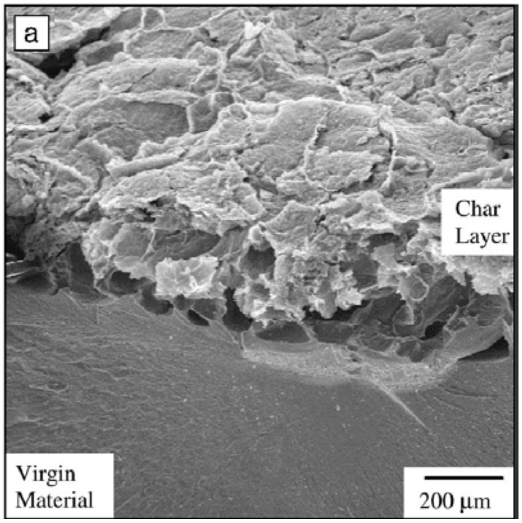

Figure 3: Demonstration of polymer/layered-silicate nanocomposite self-passivation behavior. Scanning electron micrograph of the surface of a nylon6/ 5wt% montmorillonite nanocomposite after exposure to simulated solid-rocket motor exhaust (by Vaia et.al. from [15]).

In support of these results, recent studies of nylon 6/ mmt nanocomposites by R.A. Vaia [15] found a similar fire retardancy enhancement through char formation. Specifically, the nanocomposites showed the formation of a tough ceramic passivation layer on the polymer surface, when exposed to solid-rocket motor exhaust and plasma environments (figure 3, [15]).

The above results render the finely dispersed layered silicates as a generally applicable antiflammability additive for commodity polymers, and motivate further investigations of other relevant nanocomposite properties, such as barrier properties and thermal stability.

BARRIER PROPERTIES

Superior barrier properties of polymer/layered silicate nanocomposites against gas and vapor transmission have resulted in applications for food and beverage packaging, and for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems. Theoretically a very strong decrease of gas and liquid permeabilities is predicted [19], just by considering the permeant molecule's path around the filler particles [figure 4(inset)]. The increase in path tortuosity as the small gas/liquid molecules have to diffuse around the impermeable solid fillers results in huge increases of the diffusion time, especially when fully exfoliated and oriented particles are considered [19].

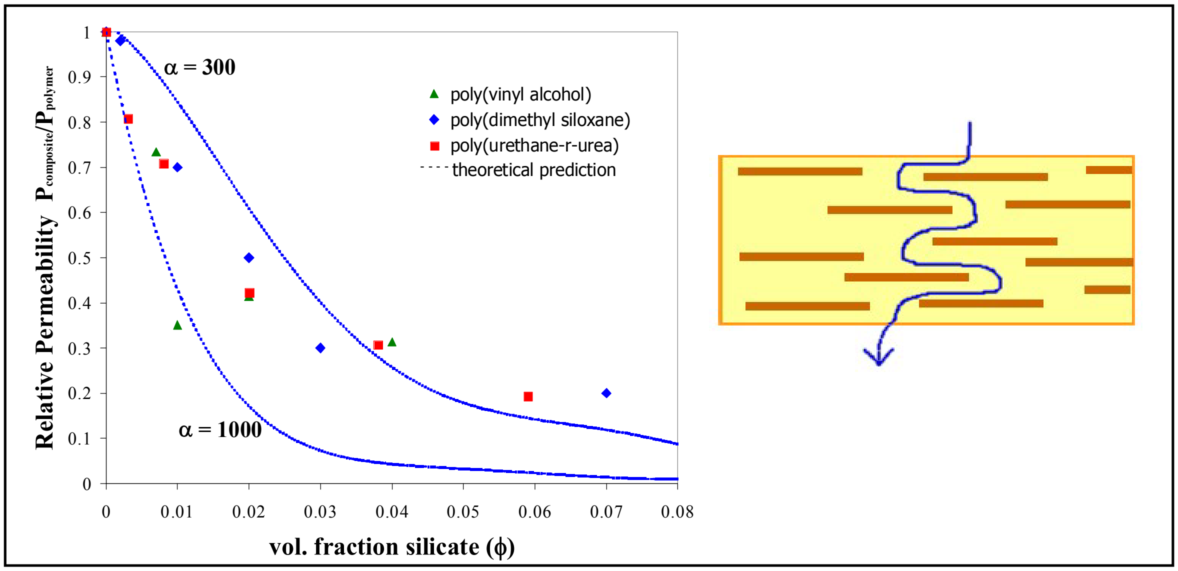

Figure 4: The relative permeability (permeability of composite divided by permeability of pure polymer) is plotted versus the volume fraction of the nm-thin inorganic filler. Water vapor permeability is measured for various systems and was compared with the theoretical predictions for filler aspect ratios of α=1000 (completely exfoliated hybrid) and α=300 (mixed exfoliated/intercalated structure). Systems span the range from very hydrophilic (polyvinylalcohol and Na^+-mmt [16]), to very hydrophobic (poly(urethane urea) and dimethyl-dioctadecyl-ammonium mmt [17]).

Experimentally, a general decrease is also found in the gas and liquid permeabilities, as for example in the case of water vapor permeation through various polymer/mmt nanocomposites (figure 4). Even when the nature of the polymer and filler is varied from extremely hydrophilic (as poly(vinyl alcohol) and Na^+-mmt [16]), to very hydrophobic (as poly(urethane urea) and dimethyl-dioctadecyl-ammonium mmt [17]), or even crosslinked systems (as PDMS networks reinforced by alkyl-ammonium mmt), all of them show a dramatic decrease in water vapor transmission [figure 4]. Compared to the theoretical predictions the permeabilities fall between the behavior of a completely exfoliated nanocomposite (filler aspect ratio α=1000) to a nanocomposite which is intercalated (α=300), and in each case traces the mixed exfoliated/intercalated structure of the hybrids [16, 17].

The same argument can also be made for the char formed in the surface of a polymer/ layered-silicate composite during combustion, and it is expected that the effect therein would be magnified due to the higher concentration of solid fillers (some of the polymer has been burned) and their expected alignment parallel to the virgin surface during combustion.

IMPROVED THERMAL STABILITY DUE TO FILLERS

The nano-dispersion of mmt in a polymer matrix also promotes an improved thermal stability, which manifests through a higher heat deflection temperature (HDT [20]) and accompanying decrease of the coefficient of thermal expansion. This improvement of the HDT originates generally from the better mechanical stability of the nanocomposite, compared to the pure polymer, rather than any increase of the polymer melting point or glass transition temperature. This general improvement is qualitatively different from the behavior of some polymers (e.g. nylon-6), where the mmt layers stabilize a different crystalline phase than found in the bulk polymer, with higher melting point and also higher HDT [21].

The purely "mechanistic" effect of these fillers on the thermal stability of the polymers can be nicely demonstrated through the example of PP/mmt nanocomposites. In all the PP/mmt hybrids studied, the melting temperature does not change markedly from that of the respective neat polymer [18]. However, there is a marked increase of the HDT, from 109°C for the neat polymer to 152°C for a 6 wt.% f-mmt 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 dependence of the HDT on the processing conditions during the composite formation, similarly to the tensile properties.

Organo-mmt filler loading $\phi_{\mathrm{o-mmt}}$ [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

Table 1: Heat Deflection Temperatures (HDT [20]) of PP/mmt nanocomposites and the respective unfilled (neat) PP. The f-mmt are mmt modified by semi-fluorinated alkyl surfactants [18]. Table from data published in [18].

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.

Concurrent to this HDT increase are also accompanying improvements in the coefficient of thermal expansion and the coefficient of thermal transmission [4]. Even more so in the case of the char formed at the surface of the polymer/silicate hybrids upon combustion, where the concentration of the fillers is locally much higher than in the nanocomposites, these properties are also expected to be affected in the same way and to a greater quantitative degree.

INSIGHTS AND PERSPECTIVE

From the above brief discussion it seems that a general mechanism underlies the flame retardant character in polymers filled by layered silicates. This mechanism is connected with the formation of a char layer, which develops on the outer surface of the composite during combustion. This surface-char has a high concentration of mmt layers and becomes a thermal insulator and a mass transport barrier (slowing the O_2 supply as well as the escape of the combustion products generated during decomposition). The formation of this char takes place under various combustion conditions, such as cone calorimetry, exposure to plasma or hot rocket exhaust. The creation of this "protective" surface char seems to require delamination –even partial– of the layered fillers, and is sensitive to the chemical details of the polymer and the surfactant.

Since the barrier and thermal stability characteristics are also general across a wide range of polymer/layered-silicate nanocomposites, it is expected –and studies to date confirm this expectation– that the operation of the layered silicate fillers as fire retardant additives should be generally applicable across many polymers. One exception seems to be polymers with reactive oxygen-containing groups (figure 2), and this is an open question for future research. Moreover, since the mechanism of flame retardancy in these composites is "mechanistic" in nature, one expects that they should work synergistically with other flame retardants "chemical" in nature (e.g. DBDPO/Sb_2O_3), and/or with oxygen scavengers. This synergy is now under investigation with very promising preliminary results.

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Experimental Details

Synthesis of nanocomposites.- All the nanocomposites presented in this paper were synthesized by blending appropriately modified layered silicates with high molecular weight polymers in absence of solvent (melt processing approach). The details for the surfactant selection and the conditions of mixing/blending are given in detail in other papers; namely for polypropylene in [10, 18], for polystyrene in [10], for epoxies [12, 13]. For poly(vinyl alcohol) and poly(urethane-urea) a co-suspension of polymers and fillers was first created in a common solvent (water and THF, respectively) and the nanocomposites were cast from this solution [16, 17]. All polymers, with the exception of the functionalized PP that were synthesized by us [18], are commercial materials and the providers are mentioned in the respective references.

Montmorillonite.- Although there exist many different natural and synthetic clays, dispersible in most polymers, due to its commercial availability montmorillonite (mmt) has become the widest used layered-silicate. 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. In their pristine form their excess negative charge is balanced by hydrated cations (Na^{+}, Li^{+}, Ca^{+2}) in the vdW interlayer. Obviously, in this pristine state mmt is only miscible with hydrophilic polymers, such as poly(ethylene-oxide) and poly(vinyl-alcohol) [16]. In order to render mmt miscible with other polymers it is required to exchange the alkali counterions with cationic-organic surfactants, e.g. alkyl-ammoniums [3, 4].

Fluorohectorite.- A synthetic 2:1 silicate, whose characteristics are much better defined than any naturally occurring silicate. Its lateral layer dimensions have a much narrower distribution than the naturally occurring mmt, and with typical lateral dimensions of $\sim 5\mu$m. Its cation exchange capacity is 1.50 meq/gr. The material was provided by Dow-Corning [10].

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