

Fire Retardant Halogen–Antimony–Clay Synergism in Polypropylene Layered Silicate Nanocomposites[†]

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Nanocomposites of polypropylene-*graft*-maleic anhydride with organically modified clays have been prepared and characterized by X-ray diffraction and transmission electron microscopy. Their combustion behavior has been evaluated using oxygen consumption cone calorimetry. Synergy is observed between the nanocomposite formed and conventional vapor phase fire retardants, such as the combination of decabromodiphenyl oxide and antimony oxide. The presence of bromine and antimony does not affect the heat release rate curves of the virgin polymer.

Introduction

Inorganic fillers are commonly added to polymers to increase their strength or impact resistance, or improve other properties, such as electrical conductivity or permeability to gases, for example, oxygen and water vapor.¹ These beneficial effects have for some years been optimized in a new class of composite materials known as polymer-layered silicate nanocomposites (PLSNs),^{2–5} which are a hybrid composed of an organic phase and an inorganic phase dispersed in the matrix in the form of reticular layers of crystals of nanometer dimension. This nanoscopic dispersion is achieved by using layered silicates (also called phyllosilicates), such as montmorillonite, vermiculite, hectorite, fluorohectorite, saponite, and so forth,^{6,7} which are rendered organophilic by replacement of the metal ions that normally balance the

negative charges with organic cations carrying an aliphatic chain, typically alkylammonium or alkyl phosphonium salts. This also increases the space between the layers and thus promotes interactions of the modified phyllosilicate with the polymer.

The study of PLSNs has become even more attractive by recent demonstrations of their flame retardant properties, namely a significant decrease in the peak heat release rate (PHRR), a change in the char structure, and a decrease in the rate of mass loss during combustion in a cone calorimeter.^{8–11} Prior to the introduction of this calorimeter, however, flame retardants were evaluated by other testing methods using very different combustion scenarios, such as the limiting oxygen index (LOI)¹² and the vertical burning test (UL94).¹³ The literature data show that, in tests of this kind, nanocomposites do not perform better than the polymer, either alone or loaded with inorganic fillers or conventional diluents, and they sometimes show poorer performance.¹⁴ Historically, fire retardant materials were developed without any reliance on cone calorimetry; rather, measurements such as the oxygen index, the UL94 test, and so forth were used.

It was therefore decided to determine whether the addition of conventional retardants, namely the combination of decabromodiphenyl oxide (DB) and antimony

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Table 1. Sample Identification and Composition

identification	composition
PPg	PpgMA
PPg/DB	PpgMA + DB 22 wt %
PPg/AO	PpgMA + AO 6 wt %
PPg/DB-AO	PpgMA + DB 22 wt % + AO 6 wt %
PPg-n	PpgMA + clay MTET ₂ 5 wt %
PPg-n/DB	PpgMA + clay MTET ₂ 5 wt % + DB 22 wt %
PPg-n/AO	PpgMA + clay MTET ₂ 5 wt % + AO 6 wt %
PPg-n/DB-AO	PpgMA + clay MTET ₂ 5 wt % + DB 22 wt % + AO 6 wt %

trioxide (AO), to nanocomposites leads to satisfactory performance in both the cone calorimeter and "traditional" tests. The low combustion rate of the polymer in nanocomposites could reduce the amount of halogenated additive needed to reach a satisfactory degree of retardancy, thus, perhaps, reducing the adverse effects that have led to a general tendency to replace halogen fire retardants. A study has therefore been made of the flammability of a polypropylene nanocomposite (polypropylene (PP) nanocomposites are actually prepared from polypropylene-*graft*-maleic anhydride) in the absence and the presence of both DB and AO. In this paper we report the results of a study of this system using cone calorimetry as the evaluative tool. The identification and composition of the various systems that have been studied are shown in Table 1.

Experimental Section

Materials. Polypropylene-*graft*-maleic anhydride (PP-*g*-MA) was obtained from the Aldrich Chemical Co. and contained 0.6% maleic anhydride (w/w) with a melting point of 152 °C and a melt flow index of 115 g/600 s, which corresponds to a $M_w = 10\,000$ uma. The phyllosilicate used to prepare the nanocomposites was kindly provided by Southern Clay Products, Inc. The ammonium cation on the clay contained a methyl group, M, tallow, T (containing 70, 25, 4, and 1 mol % of C18, C16, C14, and C12 carbon chains, respectively), and two hydroxyethyl groups, Et, which should favor wettability of the clay by the maleic anhydride units grafted onto PP; the composition is shown as MTET₂. The brominated flame retardant used is Saytex 102 E (DB 78.2% w/w and nonabromodiphenyl oxide 21.8% w/w) from Albemarle Corp., while the antimony oxide was Fireshield-H (AO 99.6% w/w and arsenic 0.4% w/w) from Laurel Industries, Inc.

Samples (Table 1) were prepared by mixing the polymer and the additives at 160 °C in a Brabender internal mixer for 30 min under nitrogen flow, followed by annealing under vacuum for 12 h at 100 °C.

X-ray scattering measurements were performed using a Rigaku powder diffractometer, with a Cu tube source ($\alpha = 1.54$ Å) operated at 1 kW. Bright field transmission electron microscopy (TEM) images of polypropylene/layered silicate (clay) nanocomposites were obtained at 120 kV, at low dose conditions, with a Phillips 400T electron microscope. The samples were ultramicrotomed with a diamond knife on a Leica Ultracut UCT microtome at room temperature to give 70 nm thick sections. The sections were transferred from water to carbon-coated Cu grids of 200 mesh. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required. Mechanical testing was performed on an Instron apparatus.

Combustion. Combustion behavior was assessed according to the ASTM E 1354-92 procedure in a Stanton-Redcroft Thermal Science Instruments cone calorimeter. During the test, the materials were subjected to irradiated heat plus the feedback heat from the flame starting from the ignition of the volatile products (ignition time). The aim was to simulate the conditions likely to occur in a real fire. The samples were

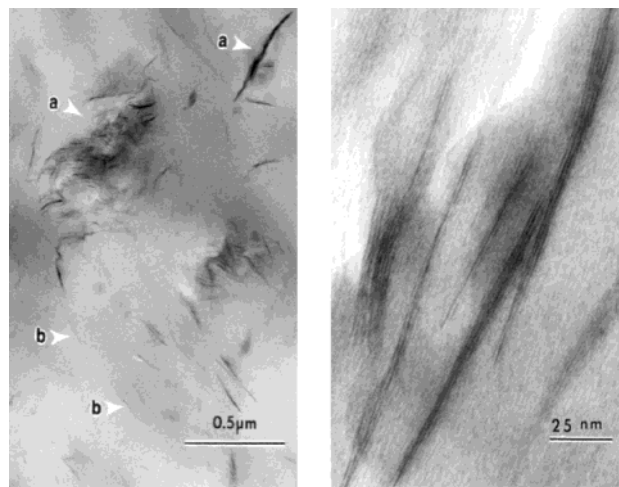


Figure 1. TEM of the PP-*g*-MA nanocomposite containing AO and DB.

irradiated at 35 kW/m², and the data were collected for the first 250 s, this being regarded as representative of the initial stage of a fire when it can still be stopped before becoming uncontrollable after flashover.¹⁵ The exhaust gas flow rate was 24 L/s. The heat released was calculated from the consumption of oxygen due to combustion.¹⁶ The mass of the sample, the mean mass loss rate, the ignition time (TTI, s), and the heat release rate (HRR, kW/m²) and its peak value (PHRR, kW/m²) were obtained directly from the software. Two other parameters were calculated separately: the TTI/PHRR, known as the "fire performance index" since it is related to the time available for flashover,¹⁷ and the average heat release rate (AvHRR), obtained by averaging the HRR in the first 180 s of combustion. The average heat release rate is correlated to the heat released in a room where the flammable materials are not ignited at the same time.¹⁸ The results from cone calorimetry are considered reproducible to within about $\pm 10\%$.¹⁹

Results and Discussion

1. Nanocomposite Characterization. The TEM images of the PP-*g*-MA composite with the MTET₂ clay, in the presence of DB and AO, are shown in Figure 1. In the image on the left, the position marked a shows the presence of intercalated clay tactoids while the position marked b shows single clay layers. In the higher magnification image on the right, one can see the intercalated clay tactoid. The XRD diagram shows a peak corresponding to an interlayer distance of 1.70 nm, which is smaller than that of the organoclay (1.88 nm). This indicates that partial decomposition of the organic alkylammonium modifier occurs during processing,²⁰ which leads to the collapse of the organoclay interlayer distance. Indeed, this would lead to the loss of the ammonium salt and its replacement with a proton, with a necessary decrease in *d* spacing.²¹ If one were to rely only on the XRD measurement, one would

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Table 2. Mechanical Properties of the Materials in This Study

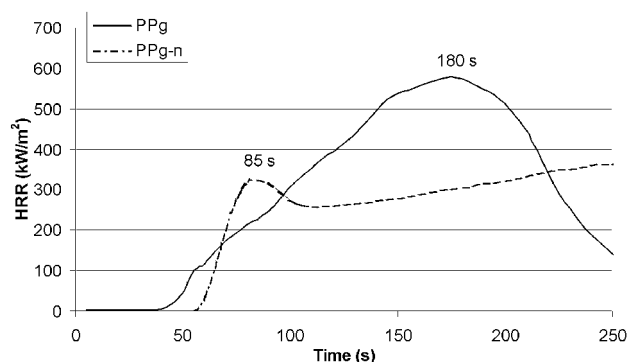
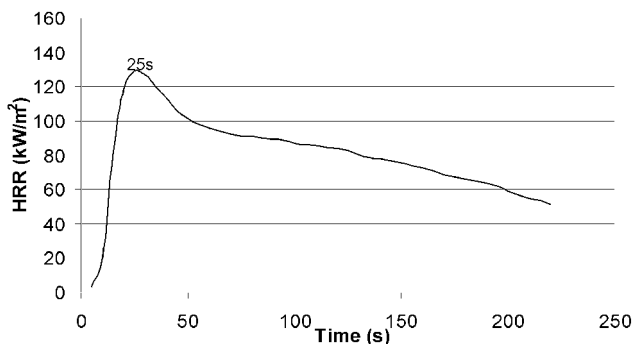
sample	yield stress (MPa)	elongation at break (%)	storage modulus (MPa)
PPg	16.9	5.4	462
PPg/DB	15.1	4.2	628
PPg-n	20.1	4.2	955
PPg-n/DB-AO	23.3	3.8	950

conclude that a nanocomposite had not been formed. It is essential to have both XRD and TEM data to characterize a nanocomposite.

Further evidence of the nanostructure of the composite is shown in Table 2, which shows the yield stress, elongation at break, and storage modulus for the systems that have been studied. There is a 100% increase in the modulus, comparing the polymer (PPg) and the nanocomposite (PPg-n); this behavior is typical of nanocomposites.²² A simultaneous reduced effect of the filler on toughness is observed, since elongation at break decreases by 1% and yield stress increases by 19%. This unusual combination of effects on mechanical properties by a filler is also an indication of nanodispersion.^{19,23} The data show that the addition of DB and AO to the nanocomposite does not have a pronounced effect on the nanostructure and the mechanical properties of the material.

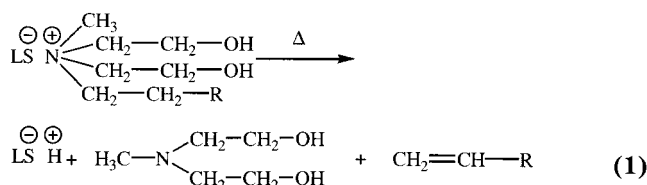
2. Combustion. *2.1. Nanocomposites.* The heat release rates (HRRs) of the polymer (PPg) and the nanocomposite (PPg-n) during the combustion tests are shown in Figure 2. When the phyllosilicate is present, the ignition time increases from 40 to 55 s. Just after ignition, however, the nanocomposite heat release rate (HRR) increases much more quickly. The heat release rate of the nanocomposite overtakes that of the polymer after 70 s (HRR = 170 kW/m²), peaks at 330 kW/m² after 85 s, and then falls much lower after 100 s (300 kW/m²). The heat release rate of the polymer rises regularly to a maximum of 600 kW/m² after 180 s. Reduction of the peak heat release rate is a typical feature of polymer layered silicate nanocomposites, as reported in the literature.^{8,9} The combustion behavior of the nanocomposite is due to a reduction in the mass loss rate, compared to that of the polymer. This greater thermal stability stems from the chemical and physical action of the crystalline layers of the phyllosilicate dispersed in the matrix.¹⁷ The peak in the heat release rate curve for the nanocomposite at 85 s is probably due to thermal decomposition of the organic modifier of the silicate layers, resulting in the formation of volatile combustibles. The heat release rate curve of the modified phyllosilicate, in fact, shows a peak of 129 kW/m² at 25 s, shown in Figure 3. The difference between this value and the value 85 s for the nanocomposite is attributable to the limited diffusion of the decomposition products of the ammonium salt in the polymer matrix.

Thermal decomposition of the organically modified montmorillonites takes place at around 200 °C and proceeds according to the Hofmann degradation mechanism.^{24,25} The initial step is the loss of an olefin,

**Figure 2.** Heat release rate curves at 35 kW/m² of the polymer (PPg) and the nanocomposite (PPg-n).**Figure 3.** Heat release rate curve at 35 kW/m² for the MTet₂ organoclay.**Table 3. Average Heat Release Rate (AvHRR) and Fire Performance Index (TTI/PHRR) for Several of the Materials in This Study**

sample	AvHRR (kW m ⁻²)	(TTI/PHRR) × 1000 (kW ⁻¹ m ² s)
PPg	279	34
PPg/DB	209	88
PPg/AO	250	65
PPg/DB-OA	254	80
PPg-n	188	111
PPg-n/DB	134	206
PPg-n/AO	164	117
PPg-n/DB-OA	107	217

followed by the loss of the amine, leaving an acid proton on the surface of the montmorillonite in the place of the ammonium cation. This is shown as reaction 1.



Dihydroxyethylamine and olefins are combustibles that feed the combustion in the flame.

Despite a larger heat release rate in the early stage of combustion, the nanocomposite shows an improvement of fire behavior indices compared to those of the virgin polymer (Table 3). The average heat release rate decreases from 279 to 188 while the fire performance

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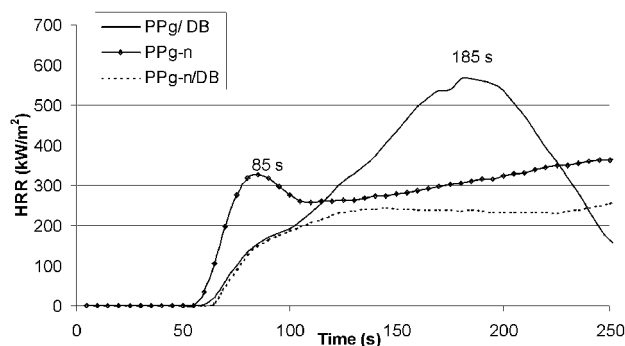


Figure 4. Effect of decabromodiphenyl oxide (DB) on the heat release rate at 35 kW/m² of the polymer (PPg) and the nanocomposite (PPg-n).

index increases from 34 to 111, owing to delay in ignition and decrease of heat release rate in a relatively short time.

2.2. Combustion of Decabromodiphenyl Oxide + Nanocomposite. The combustion pattern when 22% w/w DB is added to both the polymer, PPg, and the nanocomposite, PPg-n, is illustrated in Figure 4. The combustion curve for the polymer is virtually unchanged (cf. Figure 2); though the initial stage is slower, the ignition time increases from 40 to 60 s, so the average heat release rate falls from 279 to 209 kW/m² and the fire performance index rises from 34 to 88 (Table 3). The improved performance indicated by these indices is, however, not matched by an overall reduction of heat release rate, because the indices are strongly affected by the behavior of the material in the early stage of combustion.

Addition of DB to the nanocomposite results in a significant difference. There is a further reduction in the amount of heat released, and the peak in the heat release rate curve at 85 s disappears. This effect is due to the vapor phase fire retardant action attributable to the presence of DB, leading to a quenching of the flame.²⁶ The average heat release rate falls from 188 to 134, and the fire performance index rises from 111 to 206. The fact that the heat release rate of the nanocomposite is reduced in the presence of DB, but that of the polymer is not, may be ascribed to the slower thermal decomposition of the nanocomposite, probably due to the chemical and physical action of the crystalline layers of the clay (i.e., the barrier properties).¹⁸ The speed of the radical reactions that propagate the flame is thus low enough to allow the HBr generated by DB to slow the combustion. In the case of the pure polymer, the concentration of radicals is too high to be effectively altered by the HBr produced by DB.

2.3. Effect of Antimony Trioxide on PPg-n. Addition of metal oxides, such as AO, to halogenated fire retardants increases their efficiency through the formation of antimony trihalide, a volatile product that slows reactions in the flame, even though the oxide itself has no effect.²⁶

The heat release rate curves observed when AO is added to both the polymer (PPg) and the nanocomposite (PPg-n) are shown in Figure 5. As expected, addition to the polymer alone has no appreciable effect (cf. Figure 2) in the absence of the brominated vapor phase fire

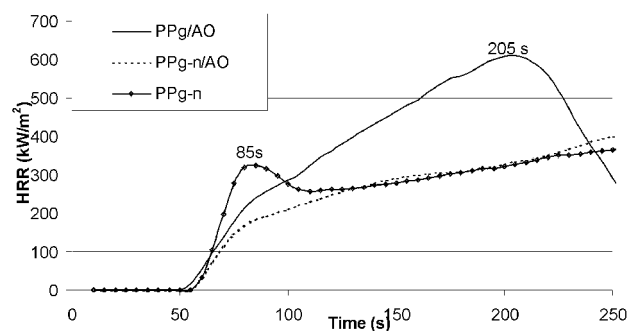
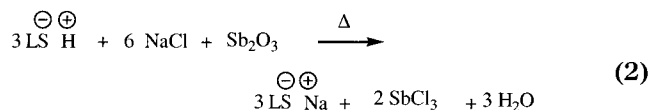


Figure 5. Effect of antimony trioxide (AO) on the heat release rate curves of polymer (PPg) and the nanocomposite (PPg-n) at 35 kW/m².

retardant. The decrease in average heat release rate from 279 to 250 and the increase in fire performance index from 34 to 65 are due to the presence of the AO filler, which reduces the fraction of combustible polymer matrix, and not to a fire retardant effect.

Addition to the nanocomposite, on the other hand, eliminates the peak at 85 s, which is due to the combustion of the decomposition products of the ammonium salt (reaction 1). This flame retarding effect is presumably attributable to volatilization of antimony trichloride formed by a reaction between AO and sodium chloride, present as an impurity in the commercial clay as a residue of clay exchange to intercalate the ammonium ion. Antimony trichloride is a well-known gas phase fire retardant.²⁶ The commercial clay has not been thoroughly washed to remove such salts.



This reaction may be catalyzed by the proton sites formed during reaction 1 on the reticular phyllosilicate layers dispersed in the matrix. By contrast with Figure 4, where the addition of DB diminished the heat release rate of the nanocomposite throughout the combustion, in Figure 5 the curves for the polymer and the nanocomposite + AO virtually coincide after about 130 s, because of the consumption of the sodium chloride needed for reaction 2 to produce the fire retardant antimony trichloride and the inert nature of AO. All three samples have the same ignition time as the polymer, 40 s (Figure 2). The marked decrease of the average heat release rate from 279 to 164 and the increase in the fire performance index from 34 to 117 (Table 3) are due once more to the sensitivity of these parameters to the initial combustion stages.

2.4. Decabromodiphenyl Oxide plus Antimony Trioxide. The combined effect of DB and AO is illustrated in the heat release rate curves for polymer with DB and AO (PPg/DB-AO), the nanocomposite with DB and AO (PPg-n/DB-AO), and the nanocomposite with only DB (PPg-n/DB) in Figure 6. The combustion of the polymer, as indicated by its peak heat release rate, is largely unchanged by the presence of the additives; the values are 580 kW/m² for the polymer alone or in the presence of only DB, 610 kW/m² in the presence of AO, and 620 kW/m² in the presence of both additives. DB alone or in combination with AO does not have a significant

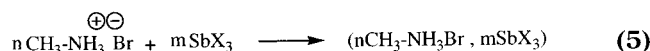
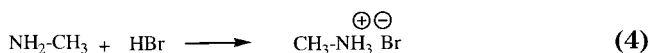
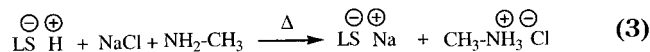
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effect on the heat release rate of PP. On the other hand, the peak heat release rate of the nanocomposite falls from 230 kW/m² for the nanocomposite alone or in the presence of DB or AO to below 200 kW/m² when DB and AO are together.

The addition of AO to the mixture nanocomposite–DB increases the heat release rate immediately after ignition at 65 s. However, the heat release rate curve of the nanocomposite combined with DB and AO reaches a plateau of 170 kW/m² after 120 s, compared with 220 kW/m² for DB alone.

The combustion parameter values for polymer plus DB and AO are much the same as those for the polymer plus DB (Table 3), while the average heat release rate for the nanocomposite plus DB and AO drops from 188 to 107 and the fire performance index rises from 111 to 217.

Figure 6 thus clearly indicates that the synergism between DB and AO demonstrated by the “historical” methods is not apparent in the polymer but can be seen in the nanocomposite, when the cone calorimeter is used as the assessment tool. Faster combustion is presumably responsible for the inability to observe the synergy in the polymer, thus nullifying the retarding effects of both the HBr generated by DB (Figure 4) and the radical inhibitor SbBr₃ generated by DB–AO. Another possibility is that SbBr₃–RNH₃Br complexes are also formed in the nanocomposite by decomposition of the organic modifier:



Complexes of this type, in fact, are much more efficient fire retardants than SbBr₃ in the case of Nylon 12.²⁷

It is well-known that the combination of DB and AO is an effective fire retardant system for polypropylene.²⁸ The observation that cone calorimetry does not show this effect is a reflection of the different types of evaluative tools that may be used to measure fire retardancy. The oxygen index and UL94 measure the ease with which a polymer may be burned or extin-

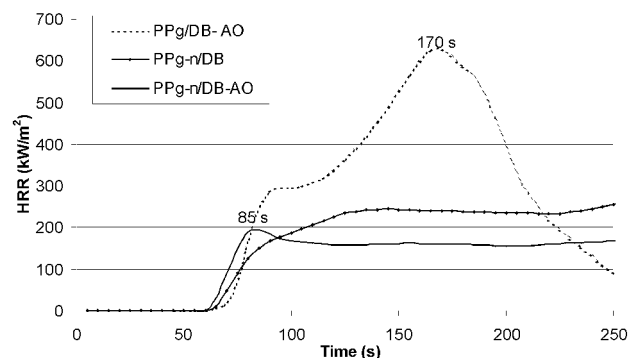


Figure 6. Effect of the combination of decabromodiphenyloxide–antimony trioxide (DB–AO) on the heat release rate at 35 kW/m² of the polymer (PPg) and the nanocomposite (PPg-n).

guished while cone calorimetry assesses the heat release rate. It is imperative that both types of information be obtained and correctly evaluated in a fire retardant study.

Conclusions

An intercalated nanocomposite is formed when the organoclay MTet₂ is melt blended with polypropylene-*graft*-maleic anhydride as shown by TEM and physical–mechanical properties. The lack of expansion of the gallery space is attributable to partial degradation of the bulky, organic ammonium salt of the organoclay during the melt blending process, giving back the more compact protonated form of the layered clay.

The nanocomposite shows a lower peak heat release rate than does the virgin polymer, which is typical of a polymer layered silicate nanocomposite and might indeed be used as a characterization tool for the formation of a nanocomposite. The peak heat release rate is reduced still further when antimony oxide or decabromodiphenyloxide is present. When both additives are present, a synergistic effect results which does not occur under identical testing conditions when antimony oxide and the brominated fire retardant are added to the virgin (i.e., PP-*g*-MA) polymer.

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