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Fire retardancy of bis[2-(methacryloyloxy)ethyl] phosphate modified poly(methyl methacrylate) nanocomposites containing layered double hydroxide and montmorillonite

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Abstract

[Copolymer nanocomposites](#) were prepared by suspension copolymerization of bis[2-(methacryloyloxy)ethyl] [phosphate](#) and [methyl methacrylate](#), together with bis(2-ethylhexyl) phosphate [layered double hydroxide](#) and a [montmorillonite](#), Cloisite 93A. X-ray diffraction and [transmission electron microscopy](#) were used to characterize the morphology of nanocomposites and the dispersion of additives in the polymer. The [thermal stability](#) of the nanocomposites has been assessed by [thermogravimetric analysis](#) and [cone calorimetry](#) has been used to study the fire properties. Bis[2-(methacryloyloxy)ethyl] phosphate not only copolymerized with MMA, but also aids in the dispersion of additives in PMMA. The copolymer nanocomposites have better dispersion and higher degradation temperature and more char mass than the corresponding PMMA nanocomposites. The largest peak reduction in the heat release rate of the copolymer nanocomposites are 52 and 65% for LDH and MMT additives, respectively.

Keywords

Nanocomposites; Layered double hydroxides; PMMA; Fire retardancy

1. Introduction

Poly(methyl methacrylate) (PMMA), a hard, rigid, transparent, and rather fragile polymer, is widely used, mainly due to its good optical properties, outstanding mechanical properties, high [thermal stability](#), and excellent electric performance. On the other hand, it is known that PMMA is highly combustible and flame retardation is needed for many applications.

Phosphorus-containing compounds are effective [flame-retardant](#) additives. The use of [phosphorus compounds](#) as flame-retardant additives in polymers is well-established^{[1], [2]}. However, the addition of additives has disadvantages, since additives often have to be used in relatively high concentrations, leading to concomitant undesirable changes in physical and mechanical properties; additives may be leached or lost from the polymer during service, posing a potential environmental hazard^[3].

The use of reactive flame retardants, i.e., phosphorus-containing flame-retardant groups that are inherently part of the polymer backbone or covalently attached as side groups to the [polymer chain](#), may promote cross-linking and char formation during combustion; even low concentrations may suffice to provide adequate protection, and reactive flame retardants are less likely to be lost from the polymer during service.

Phosphorus-containing components have been used in the synthesis of several flame-retardant for polyesters^{[4], [5]}, [polyurethanes](#)^{[6], [7]}, and [epoxy resins](#)^{[8], [9]}. Price and coworkers synthesized several phosphorus-containing [monomers](#) that could be combined with either [methyl](#)

[methacrylate](#) or [styrene](#) to obtain phosphorus-containing polymers which had enhanced fire retardancy compared to the pristine polymers^{[10], [11]}.

During the past decade, a significant amount of work has been devoted to the utilization of organically-modified clays to prepare polymer–clay [nanocomposites](#) which can have a very significant effect on many properties, including fire, mechanical and barrier properties of the polymer. A recent book reviews the use of nano-dimensional materials in polymers^[12]. As fire retardants, these materials bring about a reduction in the heat release rate which has been ascribed to the formation of a barrier to mass transport and to insulate the polymer from the heat source^{[13], [14]}.

Among the nano-dimensional materials, most attention has been directed toward [montmorillonite](#) (MMT)^{[14], [15], [16], [17]}, since it can enhance the mechanical and fire properties, and it is commercially available and well-studied. [Layered double hydroxides](#) (LDHs) are another interesting material for nanocomposite formation. These have received considerable attention in recent years because of their special structure and properties, ease of synthesis in the laboratory, and their potential industrial uses, including as fire retardants^{[18], [19]}. The utility of [LDHs](#) comes about since one can vary the identity of the metals, the [anions](#) and the [stoichiometry](#) to ascertain how these affect the ability of the [nano-material](#) to disperse in a polymer and to determine what effect dispersion has on the fire properties of the polymer^{[20], [21], [22], [23], [24]}.

Previous work from these laboratories showed that when 5% of a phosphate-containing LDH was used, one could obtain a 33% reduction in the peak heat release rate, PHRR^[23], while Price et al. obtained a 30% reduction for the phosphorus-containing [methacrylate copolymer](#) alone^{[10], [11]}. The *raison d'être* for this work is to combine these two materials to investigate possible synergistic interactions between the additive and the copolymer.

2. Experimental

2.1. Materials

Al(NO₃)₃·9H₂O (reagent grade), Mg(NO₃)₂·6H₂O (reagent grade), NaOH (reagent grade), poly(methyl methacrylate) (reagent grade), with typical *M_w* 120,000, monomeric [methyl methacrylate](#), initiator [benzoyl peroxide](#) (BPO) (97%), bis[2-(methacryloyloxy)ethyl] [phosphate](#) were purchased from the Aldrich Chemical Company. Sodium bis(2-ethylhexyl) phosphate (reagent grade 97%) was obtained from TCI America. Polyvinyl alcohol (PVA) (*M_w* = 22,000) was acquired from Acros. [Montmorillonite](#) (MMT, Cloisite 93A), with basal spacing 2.24 nm, was obtained from Southern Clay Products, Inc.

2.2. Synthesis of phosphate-LDH

The phosphate-LDH was prepared by the [co-precipitation](#) method of Zhao et al. with modification^[25]. The process has been previously described^[23].

2.3. Synthesis of copolymer–clay nanocomposites

The [copolymers](#) of MMA and copolymer–clay nanocomposites were synthesized following a literature [suspension polymerization](#) method with minor modifications^[15]. In a 3000 mL round bottom flask were placed 1000 mL H₂O, and 1 g poly(vinyl alcohol) PVOH, and this mixture was stirred for 1 h at 95 °C, then the temperature was decreased to 85 °C. In a 500 mL beaker were placed 200 mL

MMA [monomer](#), 1 g BPO, and 52 mL bis[2-(methacryloyloxy)ethyl]phosphate. After this mixture was cooled to 0 °C, 6 g, 10 g, or 20 g of phosphate-LDH or MMT Cloisite 93A was added with magnetic stirring to obtain a homogeneously [dispersed system](#). The clay–MMA–initiator mixture was added dropwise to the water–PVOH system, and the contents were stirred at 75 °C for 2 h, 85 °C for 2 h and then 95 °C for 2 h. The system was allowed to cool for 1 h with stirring and sit for 24 h. The composites were repeatedly washed with water and [methanol](#), air-dried and then dried in a vacuum oven at 100 °C for 24 h. The reaction products are identified as SusCoPMMA, SusCoPMMA + LDH and SusCoPMMA + MMT. The PMMA [homopolymer](#) and its [nanocomposites](#) were synthesized by a similar method without the addition of the phosphate-containing comonomer. These reaction products are identified as SusPMMA, SusPMMA + LDH and SusPMMA + MMT. The [phosphorus](#) content of suspension copolymerized PMMA and its char after [calcination](#) at 800 °C for 12 h are 5.9% and 8.1%, respectively.

2.4. Characterization

The phosphorus content in the polymers and the chars after combustion, was determined by the molybdovanadophosphonic acid method^[26]. X-ray diffraction (XRD) was performed on a Rigaku Miniflex II desktop X-ray powder diffractometer with CuK α generator ($\lambda = 0.15404$ nm); the accelerating voltage was 50 kV at a current of 20 mA. Scans were taken at $2\theta = 2-70^\circ$ at 0.1 step size. [Polymer composite](#) samples were pressed into $20 \times 15 \times 1$ mm³ thick plaques by [compression molding](#). The [transmission electron microscopy](#) (TEM) images were carried out using a JEOL 1230 transmission electron microscope at an accelerating voltage of 100 kV. [Thermogravimetric analysis](#) (TGA) was performed on an SDT 2960 instrument at the 12–14 mg scale under a flowing [nitrogen](#) atmosphere at a ramp rate of 20 °C/min. All TGA samples were run in duplicate and the average values are reported; the reproducibility of temperature is ± 2 °C and mass is reproducible to $\pm 0.4\%$. [Cone calorimetry](#) was performed on an Atlas CONE-2 according to ASTM E 1354 at an incident flux of 50 kW/m² using a cone shaped heater, exhaust flow was set at 24 L/s; all samples were burned in triplicate. Cone samples (about 30 g) were prepared by compression molding into $100 \times 100 \times 3$ mm³ square plaques. Based on thousands of samples that have been run, cone measurements are considered to have error bars of $\pm 10\%$.

3. Results and discussion

3.1. Morphological characterization

The morphology of these materials was evaluated by the combination of X-ray diffraction (XRD) and [transmission electron microscopy](#) (TEM). From XRD measurements, one can either observe a shift and/or broadening, or the disappearance of the peak. If a peak is observed shifted to lower values of 2θ , this is typically indicative of intercalation. If the peak does not shift and remains sharp, this likely means that the clay is simply present as an additive without any enlargement of the gallery space. Finally, if the peak vanishes or is significantly broadened, this is indicative of some disordering which could either suggest disordering without insertion of the polymer between the clay layers, a microcomposite, or disordering accompanied by polymer insertion, exfoliation.

The X-ray traces of the PMMA [nanocomposite](#) synthesized with the different additives are shown in [Fig. 1](#). Two types of additives, [phosphate](#) LDH ([Fig. 1A](#) and B) and [montmorillonite](#) Cloisite 93A ([Fig. 1C](#) and D), were used in the preparation of nanocomposites. From [Fig. 1A](#), the basal spacing (d_{003}) of HDEHP-LDH, 2.34 nm, does not change upon [suspension polymerization](#) of the

PMMA [homopolymer](#) nanocomposite, but the peak is weak, indicative of disordering. The same result is seen for the [copolymer](#), [Fig. 1B](#); the XRD results indicate that TEM is required to evaluate the morphology of these systems.

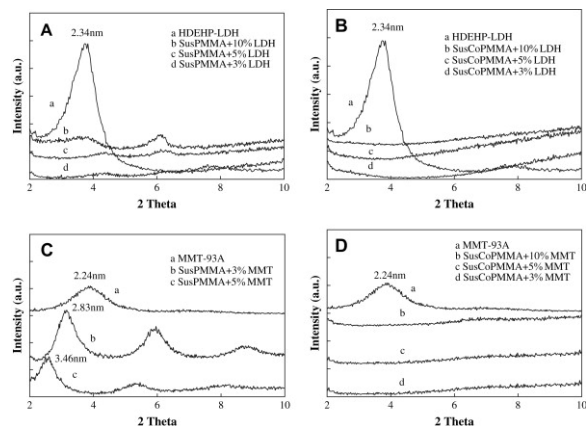


Fig. 1. XRD traces of suspension polymerized MMA with HDEHP–LDH (A); suspension copolymerization of MMA with the phosphorus-containing comonomer (B); [suspension polymerization](#) of MMA with MMT (C); and (D) suspension copolymerization of MMA with the phosphorus-containing comonomer and MMT (D).

For the montmorillonite series ([Fig. 1C](#) and [D](#)), the first order basal reflection of montmorillonite Cloisite 93A corresponds to a basal spacing of 2.24 nm. Upon suspension polymerization at 3% additive loading, the (001) basal reflection is sharper and shifts to 2.83 nm. At 5% Cloisite 93A loading, the (001) basal reflection is again broader than in the pristine clay, but not as sharp as at 3% loading and the peak is shifted to 3.46 nm ([Fig. 1C](#)). Second order reflections, indicative of increased ordering, are also seen. The indication from XRD is that intercalated systems have been produced, possibly with some disordering. It was not possible to synthesize a PMMA nanocomposite containing 10% MMT because this large an amount of MMT cannot be well-dispersed in the PVOH solution of the [monomer](#). When the two comonomers, phosphate-containing and MMA, were solution polymerized in the presence of 3, 5 and 10% Cloisite 93A loading, the (001) basal reflection disappeared entirely ([Fig. 1D](#)), which again indicates the need for TEM. It is interesting to note that when the phosphorus-containing comonomer is present, one can disperse 10% clay.

Typically two [TEM images](#) are presented, one at low magnification to see the global dispersion of the clay in the polymer and one at high magnification to permit a description of the system. [Fig. 2](#) shows the TEM images of phosphate-containing [LDHs](#) in PMMA ([Fig. 2](#) top) and in the copolymer ([Fig. 2](#) bottom). From the lower magnification images, on the left, the global dispersion is better in the copolymer than in PMMA, but both of these should be described as microcomposites.

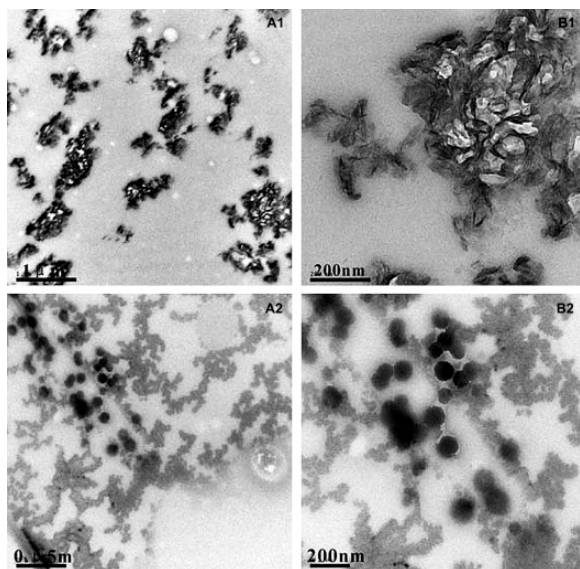


Fig. 2. [TEM images](#) for [suspension polymerization](#) of PMMA with HDEHP-LDH; (A1, B1) and suspension polymerization of MMA with the phosphate-containing comonomer with HDEHP-LDH (A2, B2).

The TEM images of the MMT systems are shown in [Fig. 3](#). For both PMMA and the copolymer nanocomposites, the low magnification images show that good dispersion has been achieved. In the right top of [Fig. 3](#), labeled as B3, one can see the intercalated nature of this PMMA-MMT nanocomposite. For the copolymer-MMT system, the high magnification image, labeled B4, shows the random arrangement of the clay layers, indicative of exfoliation. These TEM results are consistent with the XRD results.

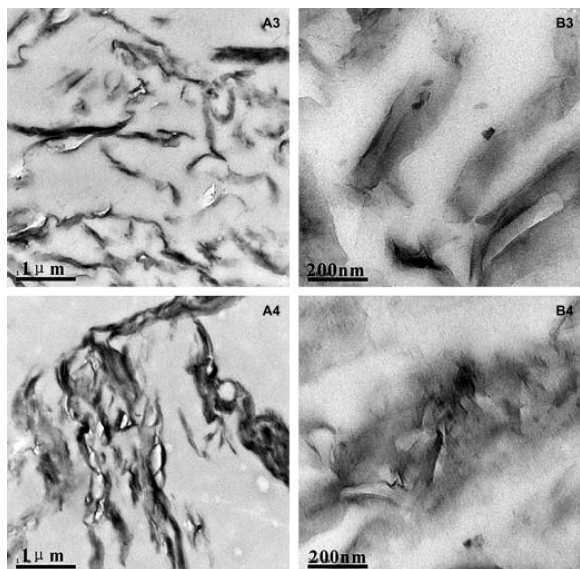


Fig. 3. [TEM images](#) of [suspension polymerization](#) of MMA with MMT (A3, B3) and MMT and suspension polymerization of MMA with the phosphate-containing comonomer with MMT (A4, B4).

3.2. Thermal degradation behavior

[Thermogravimetric analysis](#) (TGA) of polymers enables a description of the degradation process. The points of interest are the onset temperature of the degradation, typically taken as the point at which 10% degradation occurs, $T_{0.1}$, the mid-point of the degradation, $T_{0.5}$, and the fraction of char which remains at the conclusion of the run. All of this data is reported in [Table 1](#) and the TGA curves as well as the derivatives, DTG, are shown in [Fig. 4](#), [Fig. 5](#).

Table 1. TGA summary results for [methacrylate](#) and methacrylate (nano)composites.

Formulation	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Char(%)
Pure PMMA	276	368	0.6
Sus PMMA	270	367	0
Sus PMMA + 5% LDH	286	326	2.1
Sus CoPMMA	332	409	2.0
Sus CoPMMA + 5% LDH	309	403	8.2
Sus PMMA + 5% MMT	303	389	7.5
Sus CoPMMA + 5% MMT	314	411	11.5

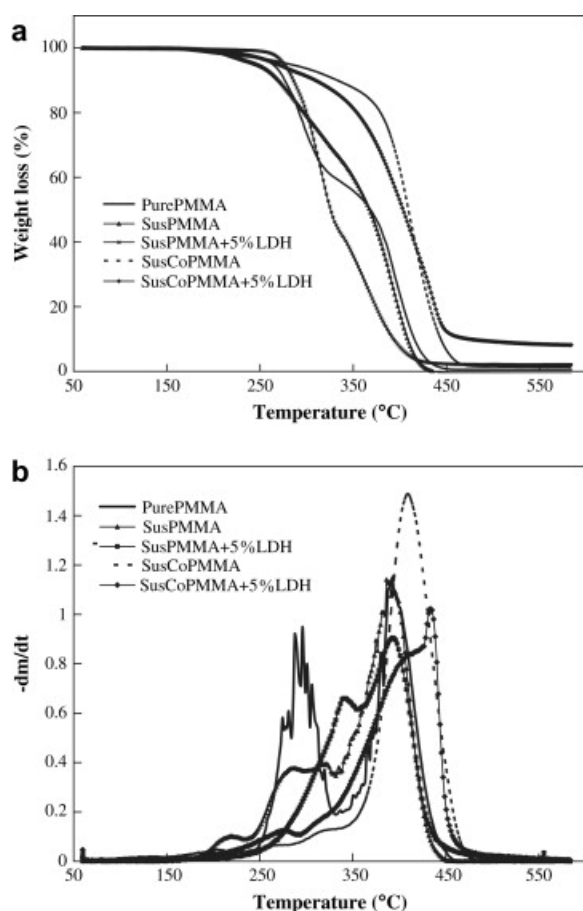


Fig. 4. TGA (a) and DTG (b) curves of PMMA phosphate-LDH [nanocomposites](#).

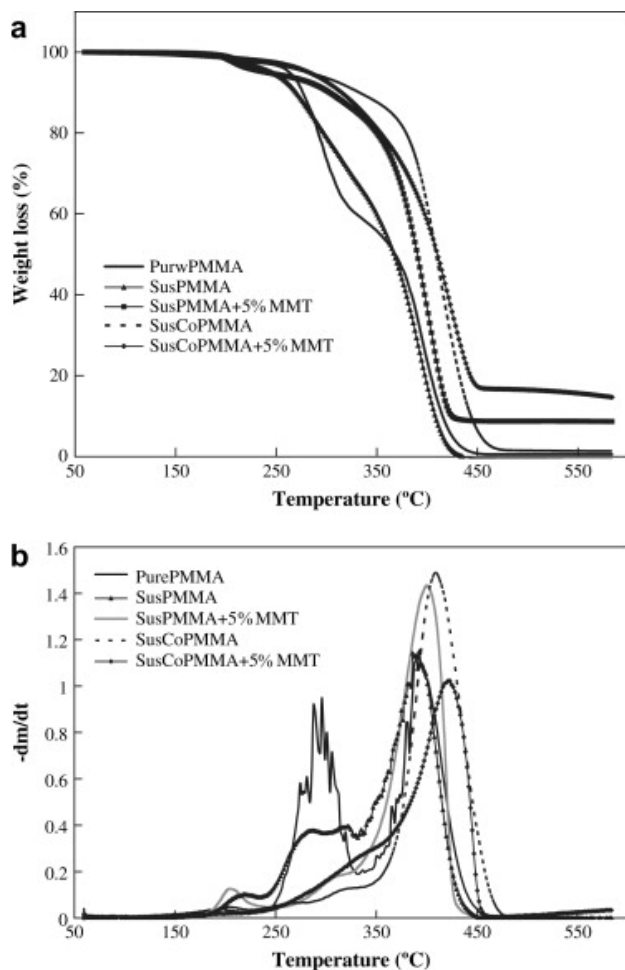


Fig. 5. TGA (a) and DTG (b) curves of PMMA-MMT [nanocomposites](#) (B).

The thermal degradation of PMMA is well-understood and consists of three steps, attributed to cleavage of weak links, i.e., head-to-head linkages^[27], and then a larger mass loss due to end chain unsaturation and the final event, which accounts for the majority of the degradation, is due to random scission^[28].

The copolymer and copolymer nanocomposites begin thermal degradation above 250 °C, and at a much slower rate than the melt blended commercial PMMA. The degradation rapidly increases after 350 °C, which is much higher than that of pristine PMMA. The onset and 50% degradation temperatures for the copolymer are 60° and 40° higher than the corresponding suspension polymerized PMMA, indicating substantial enhanced [thermal stability](#) for the copolymer. The addition of either MMT or LDH at 5% loading to this copolymer brings about a reduction in the onset temperature, probably due to the presence of the less stable additive.

3.3. Fire retardancy of the nanocomposites

[Cone calorimetry](#) is one of the most useful methods to evaluate the fire performance of polymers. The parameters that may be evaluated from cone calorimetry include the heat release rate (HRR), and especially its peak value (PHRR); the time to ignition (t_{ig}); the volume of smoke (VOS); the [total heat](#) released, (THR), a measure of the extent to which the entire polymer burns; and the average mass loss rate (AMLR). The peak heat release rate, which gives information about the size of the fire and can

be viewed as the “driving force” of the fire, is considered to be one of the most important parameters in assessing potential behavior in a real fire.

The cone calorimetric data, obtained at heat flux of 50 kW/m², are given in [Table 2](#) while the heat release rate plots are shown in [Fig. 6](#). In addition, [Fig. 7](#) shows the total heat released as a function of time while [Fig. 8](#) provides the smoke data. Both pristine, commercial PMMA and the material which was obtained by suspension polymerization give similar results but the copolymer shows a 44% reduction in the PHRR, compared to PMMA. As noted in the experimental section, the copolymer contained 5.9% [phosphorus](#) as determined by analysis. For comparison, Price et al. used a copolymer which contained 3.5% phosphorus, based upon the amounts of starting material, and observed a 30% reduction in the PHRR at 35 kW/m². It is commonly agreed that fire retardancy due to phosphorus is proportional to the phosphorus content^[29], so one may assume that the incremental decrease in the PHRR seen in this study is due to the increased phosphorus content. The total heat released is less for the copolymer compared to the homopolymer, which may be an indication that some of the material does not burn. Strikingly, the volume of smoke is approximately four times larger for the copolymer than for the homopolymer. Once again, this may likely be attributed to the presence of phosphorus.

Table 2. Cone calorimetric data for [methacrylate](#) and methacrylate (nano)composites.

Formulation	PHRR (kW/m ²)	Reduction(%)	THR (MJ/m ²)	VOS (L)	AMLR (g/s m ²)	t _{ig} (S)	t _{PHRR} (S)
Pure PMMA	1129 ± 95	NA	86 ± 1	361 ± 25	32 ± 4	9 ± 2	72 ± 7
Sus PMMA	1081 ± 63	4	81 ± 1	376 ± 2	32 ± 1	7 ± 1	76 ± 14
Sus CoPMMA	635 ± 41	44	60 ± 1	1659 ± 8	34 ± 16	8 ± 1	62 ± 3
Sus PMMA þ 3% LDH	798 ± 76	29	83 ± 3	595 ± 100	27 ± 1	8 ± 2	101 ± 10
Sus PMMA þ 5% LDH	623 ± 42	45	73 ± 3	747 ± 15	22 ± 2	6 ± 1	80 ± 6
Sus PMMA þ 10% LDH	491 ± 18	56	73 ± 1	797 ± 60	17 ± 0	7 ± 1	65 ± 15
Sus CoPMMA þ 3% LDH	720 ± 28	36	61 ± 1	1595 ± 30	28 ± 1	10 ± 1	58 ± 28
Sus CoPMMA þ 5% LDH	680 ± 24	40	57 ± 1	1727 ± 80	26 ± 1	9 ± 1	61 ± 1
Sus CoPMMA þ 10% LDH	542 ± 20	52	63 ± 2	1647 ± 50	19 ± 1	11 ± 0	60 ± 6
Sus PMMA þ 3% MMT	539 ± 58	52	69 ± 1	730 ± 80	17 ± 1	5 ± 2	58 ± 4
Sus PMMA þ 5% MMT	538 ± 28	52	66 ± 6	654 ± 50	17 ± 0	6 ± 2	56 ± 9
Sus CoPMMA þ 3% MMT	439 ± 15	61	57 ± 1	1611 ± 110	13 ± 5	11 ± 3	87 ± 5
Sus CoPMMA þ 5% MMT	482 ± 54	57	61 ± 2	1455 ± 55	17 ± 2	14 ± 1	81 ± 12
Sus CoPMMA þ 10% MMT	392 ± 131	65	51 ± 17	1412 ± 30	21 ± 7	15 ± 3	85 ± 8

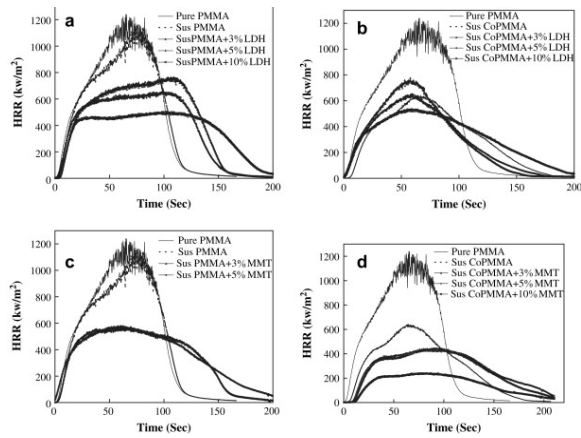


Fig. 6. HRR vs. time for (a) [suspension polymerization](#) PMMA LDH [nanocomposites](#), (b) suspension copolymerization PMMA LDH nanocomposites, (c) suspension polymerization PMMA-MMT nanocomposites and (d) suspension copolymerization nanocomposites.

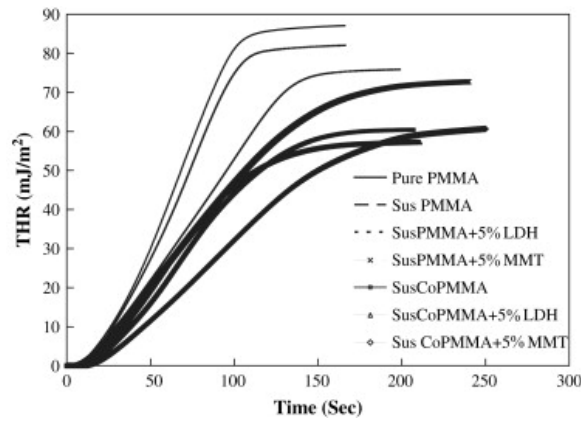


Fig. 7. THR vs. time for [suspension polymerization](#) and suspension copolymerization [nanocomposites](#).

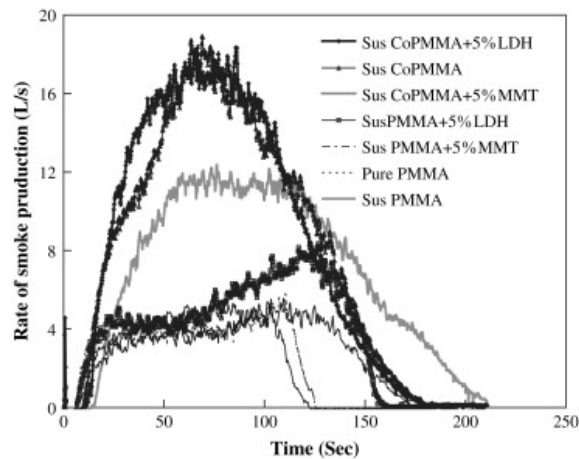


Fig. 8. Smoke evolution vs. time for [suspension polymerization](#) and suspension copolymerization [nanocomposites](#).

In previous work for these laboratories^[23], nanocomposites of PMMA with the phosphate-containing LDH have been prepared both by melt blending and by bulk polymerization. At 10% LDH, the reduction in the PHRR by melt blending was 37% vs. 31% by bulk polymerization and 56% in this work. By melt

blending, a mixed intercalated/exfoliated nanocomposite was produced but bulk polymerization gave a microcomposite and, in this work, a microcomposite was also obtained. It is obvious that there is no correlation between dispersion of the polymer in the clay and reduction in PHRR but such a correlation is well-known for MMT systems. Fire retardancy due to the addition of an LDH to a polymer may be ascribed to 1) endothermic decomposition of the constituent [hydroxides](#), 2) the presence of water amongst the combustible gases, and 3) the presence of the oxide char formed during the degradation.

Comparing suspension polymerized PMMA with the copolymer in the presence of the LDH, there is very little difference in the PHRR. While the presence of the phosphorus comonomer has a significant effect for the polymer only, when the LDH is added, there is no additional effect. There is a smooth decrease in both the mass loss rates and the PHRR as the amount of LDH increases, in agreement with the usual expectation for fire retardancy. The time to PHRR is longer for PMMA–LDH nanocomposites, compared to pristine PMMA, while it is constant for the copolymer containing LDH.

In the presence of MMT, there is very little difference between PMMA and its copolymer. The reductions in the PHRR are slightly larger for the copolymer but only slightly larger. Since the PHRR is relatively constant, one might expect that the mass loss rate would also be similar and this is observed. The usual explanation for the reduction in the PHRR is that the decrease in the mass loss rate is the cause of the reduction in the PHRR.

Normally only 3% MMT is added to a polymer because this amount has proved optimal for most purposes. In previous work, we have used between 0.1 and 5% MMT with [polystyrene](#) and found that there are only marginal differences over this concentration range^[30]. It is very surprising that for PMMA the PHRR continues to decrease as MMT is added. This suggests that the entire body of work on the various polymers with MMT must be reexamined to determine if there is a concentration effect and to determine the origin of this effect.

Barrier formation during combustion is the general mechanism invoked for fire retardancy using polymer-clay nanocomposites. Char formation and the char structure are very important for [fire retardant](#) efficiency; photographs of the char after cone calorimetry are shown in [Fig. 9](#). The char mass and structure are very different between polymer and copolymer nanocomposites. There is no char formation for either pristine, commercial PMMA or suspension polymerized PMMA, but the suspension copolymerized material containing no additive retains carbonaceous char, with a mass of 2% and a network structure ([Fig. 9C](#)). For the LDH-containing PMMA system, the char content of the composite with 5% HDEHP–LDH loading is 2.1% and only a part of the [aluminum foil](#) in which the cone sample was wrapped can be seen at the end of the run ([Fig. 9A](#)). The copolymer with 5% LDH gives 8.2% char and this covers the entire aluminum foil ([Fig. 9D](#)). Even at 3% LDH loading, the entire aluminum foil is covered with residue.

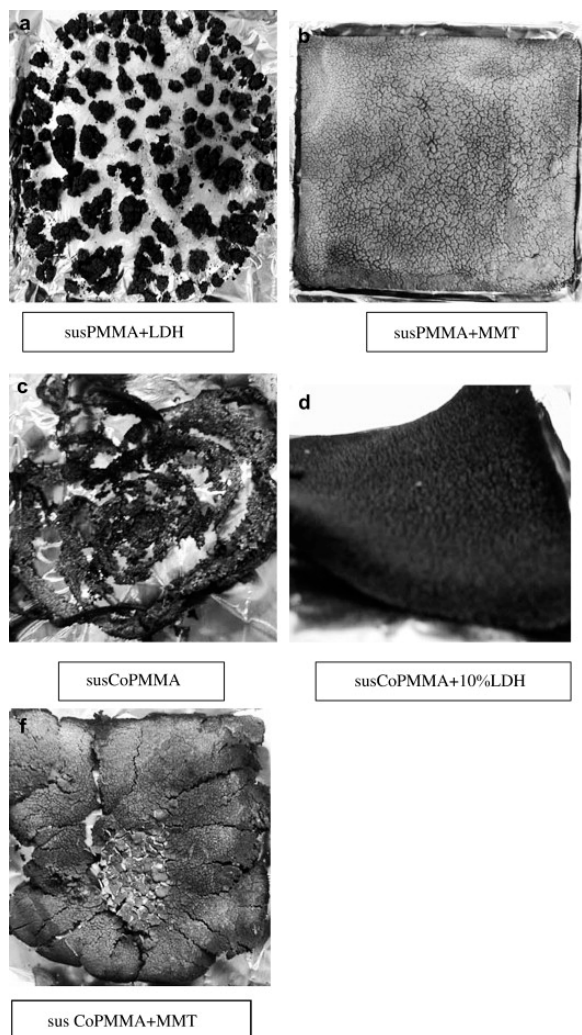


Fig. 9. Photographs of residual char from (a) susPMMA + LDH, (b) susPMMA + MMT, (c) susCoPMMA, (d) susCoPMMA + 10% LDH and (e) sus CoPMMA + MMT formulations.

The copolymer nanocomposites form a unitary char structure even at very low LDH loading (3%) and this char covers all of the aluminum foil. For the 5% MMT system, the char content for the PMMA nanocomposite is 7.5%, and the char content increases to 11.5% for the copolymer, and both have a seemingly impermeable network structure. The significantly higher char content for the copolymer nanocomposites, compared to PMMA, may imply some synergy to enhance cross-linking and the formation of carbonaceous char.

The XRD traces of the residual char after cone calorimetry shows only very weak peaks before [calcination](#); after calcination at 900 °C for 12 h, the XRD peaks sharpen and the pattern is shown in [Fig. 10](#). For SusCoPMMA with no additive, complete [volatilization](#) occurred after calcination. The main phase in the formulation sus PMMA + LDH char is [magnesium phosphate](#)($Mg_3(PO_4)_2$) with a small amount of spinel ($Mg_{0.4} Al_{0.6} Al_{1.8} O_4$). The char of copolymer nanocomposites with either LDH or MMT consists mainly of aluminum phosphate ($AlPO_4$). These data agree with analysis which shows the presence of phosphorus in the residue.

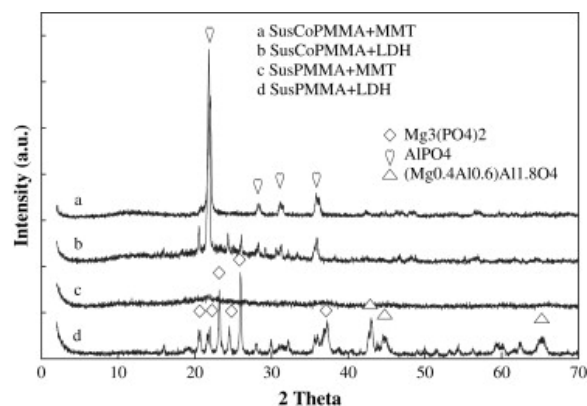


Fig. 10. XRD traces of the residual char calcined at 900 °C for 24 h.

4. Conclusions

Both the PMMA [homopolymer](#) and its [copolymer](#) with bis[2-(methacryloyloxy)ethyl] [phosphate](#) were synthesized and combined with two nano-dimensional materials, an LDH and an MMT. The presence of the phosphorus-containing comonomer enables the dispersion of the additives in the polymer. MMT is much better dispersed in both the polymer and the copolymer than is the LDH. For the systems PMMA–MMT, the reduction in the peak heat release rate continues to increase above 3% loading, which is behavior unlike that of other polymers that have been studied and suggests that there are effects in these systems that are still not understood.

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