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Fire retardancy of melamine and zinc aluminum layered double hydroxide in Poly (methyl methacrylate)

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Abstract:

The thermal and fire properties of PMMA modified with various loadings of melamine or zinc aluminum undecenoate LDH were evaluated using TGA, DTA and cone calorimetry. The additives were characterized by X-ray diffraction, TGA, FT-IR and elemental analysis. While the two additives are very effective with this polymer, a higher loading of melamine (30%) is required to reach a good reduction in PHRR (47%) relative to the pure polymer, while with the LDH, 10% loading is enough to obtain a similar reduction. The combinations of these additives in PMMA reveal that the time to PHRR and the amount of smoke produced are the key differences, with melamine increasing the first parameter and leading to less smoke production relative to LDH-rich PMMA

systems at similar total additive loadings. Analysis of the residue shows that melamine is completely lost during combustion while the LDH forms ZnO and ZnAl_2O_4 .

Keywords: Fire retardancy, Melamine, Layered double hydroxides, Nanocomposite.

1. Introduction

For the past decade, polymer nanocomposites have been an extensively studied class of materials for a variety of applications including improved mechanical properties, gas barrier performance, improved thermal properties and reduced flammability [1]. To enhance these properties, using montmorillonite (MMT) as the nano-dimensional material, the presence of a nano-scaled morphology, either an exfoliated or intercalated structure, was found to be the key point [2], 2a and 2b. The most commonly used nanomaterials are smectite-type materials containing an intercalated alkylammonium in order to reduce the surface polarity and enhance the compatibility with the polymers [3].

Typically, for polymer nanocomposites where no additional fire retardant is used, the peak heat release rate (PHRR) is greatly reduced for the materials as measured by cone calorimeter, but the total heat released remains unchanged. This means that once the polymer nanocomposite is ignited, the materials burn slowly but do not self-extinguish until most of the fuel has been combusted 2b and [4]. The reduction in PHRR is important for fire safety, as PHRR represents the point in a fire where heat is likely to propagate further, or ignite adjacent objects [5]. However, in order to pass other regulatory tests, such as the UL 94 protocol, nanocomposites alone cannot achieve a rating and they must be combined with other fire retardants [6].

Thus, in efforts to develop new materials that will perform well in cone calorimetry, but at the same time, materials that will be able to pass the regulatory tests, the effectiveness of several combinations of commercial fire retardants, like phosphates, metal hydroxides (ATH, MDH) and layered nanomaterials, have been studied in these laboratories [7], 7a, 7b and 7c. The nanomaterials most commonly studied have been the cationic organoclays, like MMT. Recently though, several other nanomaterials, layered double hydroxides (LDH)

and other layered metal hydroxides, have also been reported as potential fire retardant additive for polymers [8], 8a, 8b and 8c. Exploring these new systems and understanding their mode of action will complement the previous studies.

The purpose of this paper is to investigate the thermal and fire properties of PMMA modified with a zinc aluminum layered double hydroxide (an anionic clay), melamine (a known fire retardant) and combinations of the two. The layered double hydroxide (LDH) structure consists of brucite-like sheets, in which divalent cations are partially replaced by trivalent cations, and interlayer anions compensate for the positively charged layers. The general formula for these materials is $(M^{II}_{1-x} M^{III}_x(OH)_2)^{x+} (A^{n-})_{x/n} \cdot mH_2O]_{inter}$ where M^{III} and M^{II} are trivalent and divalent cations in octahedral sites within the OH-layers and A^{n-} is an exchangeable anion such as NO_3^- and SO_4^{2-} [9].

In recent work on layered double hydroxides (LHDs), it was shown that one can vary the identity of the divalent metal and tune the LDH to a polymer and obtain a significant enhancement in fire properties [10]. The anion has also been varied, including carboxylates, sulfates, sulfonates and phosphates, and it was found that the change in the carboxylate chain length was not important for poly(methyl methacrylate) (PMMA) systems but did make a difference with polystyrene [11]. When sulfur or phosphorus anions are used, one observes good nano-dispersion with PMMA but not with polystyrene [12]. The LDHs appear to be more compatible with PMMA than the non-polar polystyrene [13]. Particular emphasis is placed on PMMA where usually modest reductions are typical when modified with cationic clays, but greater reductions are obtained by combining this polymer with the appropriate LDH.

Attempts to combine PMMA with commercial fire retardants have always been an area of interest in the fire community. Kim has studied, for example, the combination of a PMMA nanocomposite with triphenyl phosphate [14]. It was also reported that an ammonium polyphosphate (APP)-based additive containing melamine phosphate led to an intumescent behavior during cone calorimeter tests of their PMMA composites, whereas the thermal stability was particularly improved by the use of oxide nanoparticles [15].

Levchik and Costa [16] reported improvement in fire retardancy as measured by oxygen index test and UL 94 by compounding melamine and its salts with polyamide 6 (PA-6). It has been found that melamine and its derivatives are effective fire retardants for polyamides because they cause melt dripping and extinction of the flame without combustible drops; melamines are ineffective in the reinforced PA-6, since dripping is inhibited [17]. Shimasaki et al. also found that PA-6 mixed with melamine is self-extinguishing while melamine is not effective for either polypropylene (PP) or low-density polyethylene (LDPE) [18]. Reshetnikov et al. investigated the efficiency of phosphoric acid derivatives in conjunction with pentaerythritol and/or melamine as fire retardants, and observed that the efficiency of intumescent systems depended on the thermal protection properties of the foamed char [19].

In this work, we investigate the effect of various loadings of melamine, zinc aluminum LDH, and their combinations on the thermal and fire properties of PMMA.

2. Experimental

2.1. Synthesis of the organically modified LDH

2.1.1. Materials

Most chemicals used in this study were analytical grades, obtained from the Aldrich Chemical Company, and used without further purification. These include: methyl methacrylate monomer; inhibitor remover columns; benzoyl peroxide, zinc nitrate hexahydrate; aluminum nitrate nonahydrate; 10-undecenoic acid; sodium hydroxide and melamine.

2.1.2. Preparation of the LDHs

The ZnAl LDH 10-undecenoate was synthesized by the co-precipitation method [28]. The preparation was performed in a N₂ atmosphere to exclude carbon dioxide from the LDHs. In a typical experiment, in a 3000 ml three neck flask under a flow of nitrogen to exclude CO₂, 1000 ml of distilled water was boiled for 30 min while purging it with nitrogen, then cooled to room temperature. To this

water, 0.2 mol of NaOH was added, and the mixture stirred until the NaOH dissolves completely. Then, 0.2 mol of undecenoic acid was added to the solution and the solution stirred until it was homogenous. In a separate flask, a solution of zinc nitrate (0.3 mol) and aluminum nitrate (0.1 mol) in 450 ml of degassed water was prepared. The nitrate solution was slowly added dropwise to the stirred undecenoate/NaOH solution at room temperature, maintaining the pH at the desired value (10.0 ± 0.1), using 1 M NaOH solution. After all nitrate solution was added, the resulting slurry mixture was aged for 24 h at 80 °C, filtered, washed (degassed water) and dried in a vacuum oven at 65 °C for 12 h. The resulting LDH was characterized by powder X-ray diffraction, FT-IR, elemental analysis and thermogravimetric analysis.

2.2. Preparation of PMMA composites

Nanocomposites were prepared by in situ polymerization in a two-step process. Methyl methacrylate monomer, LDH and/or melamine (the weight of monomer and additives for each sample was set at 120 g) were combined in a 400 ml beaker and covered with aluminum foil to minimize monomer evaporation. The mixture was stirred for 24 h at room temperature then 0.12 g of the initiator, BPO, (0.1%) was added, and the stirring was continued for an additional 30 min. The mixture was then heated at 60 °C until it formed a viscous paste. In the second step, BPO (0.1%) was added again to the viscous mixture after it had cooled to room temperature, and the paste was heated to 120 °C for 8 h to yield the desired polymer. The unreacted monomer was removed by heating the resulting polymer overnight in a vacuum oven at 100 °C. This two-stage process was also used for the preparation of the PMMA/melamine composites and the control PMMA experiment.

2.3. Determination of molecular weight by viscosity

The molecular weight of PMMA used in this work was obtained from viscosity data. The results are an average of three determinations, and the Mark–Houwink constants were obtained from published data [20].

2.4. Instrumentation

Fourier transform infrared (FT-IR) spectra of the solid materials were obtained using the KBr method on a Nicolet Magna-IR 560 spectrometer operated at 1-cm^{-1} resolution in the $400\text{--}4000\text{-cm}^{-1}$ region. Powder X-ray diffraction measurements (PXRD) were performed in a Rigaku, Miniflex II, Desktop X-ray diffractometer. Data acquisition was performed using a step size of 0.033° per second. Elemental analysis was carried out by Huffman Labs, Colorado, using atomic emission spectroscopy interfaced with inductively coupled plasma (AES-ICP) for metal determination. Thermogravimetric analysis (TGA) was performed on a SDT 2960 (TA Instruments) at the 15 mg scale under a flowing nitrogen atmosphere at a scan rate of $20^\circ\text{C}/\text{min}$. Temperatures are reproducible to $\pm 3^\circ\text{C}$, while the error on the fraction of non-volatile materials is $\pm 2\%$. Cone calorimeter measurements were performed on an Atlas CONE-2 according to ASTM E 1352 at an incident flux of 50 kW/m^2 using a cone shaped heater; the exhaust flow was set at 24 L/s . The specimens for cone calorimetry were prepared by the compression molding of the sample (about 30 g) into $3 \times 100 \times 100\text{ mm}$ square plaques. Typical results from cone calorimetry are reproducible to within about $\pm 10\%$; these uncertainties are based on many runs in which thousands of samples have been combusted [21].

3. Results and discussion

Fig. 1 provides the XRD patterns of ZnAl. The strongest diffraction peak appears at $2\theta = 3.12^\circ$, corresponding to a basal spacing of 2.83 nm, and an interlayer spacing of about 2.35 nm (estimating that the thickness of brucitic layer is approximately 0.48 nm) [9]. The presence of at least three equidistant reflection peaks demonstrates that the synthesis produced a layered material. Also, this larger interlayer spacing confirmed that the 10-undecenoate anion was incorporated into the gallery space of the LDH as also confirmed in later sections, by FT-IR, TGA and DTA experiments.

Fig. 2 provides the FT-IR of the undecenoate-containing LDH. From the observed band positions, this LDH contains the undecenoate anion and is similar to reported FT-IRs of LDH intercalated with this anion [28]. An additional band, a sharp band around 1596 cm^{-1} , is

also observed in this spectrum. Usually, the presence of a peak around 1596 cm^{-1} is attributed to the asymmetric $\nu_{\text{C=O}}$ of a hydrogen-bonded carboxylic acid in the interlayer of the LDH material [22] and [23]. The intercalation of such free acid groups [24] is a general phenomenon when excess carboxylate anions are used in the exchange or preparation, even at such high pH [25].

Elemental analysis of the ZnAl was also obtained. These results suggested that in addition to the charge balancing anions, the LDH also contained some protonated anions, as suggested by the FT-IR measurements. The results obtained from elemental analysis are: found for ZnAl: 30.60% Zn, 3.58% Al, 30.33% C, 6.14% H, with atomic ratio Zn/Al = 3.53; calculated for ZnAl: 30.46% Zn, 3.56% Al, 30.16% C, 6.05% H, with the formula $\text{Zn}_{3.53}\text{Al}(\text{OH})_{9.06}(\text{C}_{11}\text{H}_{19}\text{O}_2)(\text{C}_{11}\text{H}_{20}\text{O}_2)_{0.73} \cdot 1.62\text{H}_2\text{O}$. The ratio Zn/Al is slightly greater than the original solution which may be due to the presence of other minor products, like boehmite (AlOOH), precipitating along with the major LDH product.

The thermal stability of this LDH was evaluated in a TGA experiment, under a constant nitrogen environment, at a heating ramp rate of $20\text{ }^{\circ}\text{C}/\text{min}$. As observed in Fig. 3, the ZnAl LDH degrades in approximately three steps, the first two of which are likely the loss of water below $200\text{ }^{\circ}\text{C}$. The DTA curve (Fig. 4) also supports the loss of water as the primary channel of degradation with two endothermic peaks observed below $200\text{ }^{\circ}\text{C}$. This is the normal observation for an LDH [23]. The LDH slowly loses organic materials in the temperature range $250\text{--}500\text{ }^{\circ}\text{C}$, and the final mass of the char remaining after the TGA experiment was found to be 50% at $800\text{ }^{\circ}\text{C}$. Taking into consideration the instrumental error, this char was a little higher than that predicted from the elemental analysis (44.4%) which suggests that the LDH may contain some other minor amorphous products, not detectable with XRD measurements, along with the target LDH material. It must be noted that chemical analysis does not rule out the possibility of erroneous values as a result of precipitation of $\text{M}(\text{OH})_2$ and/or $\text{Al}(\text{OH})_3$ phases upon the LDH surfaces, which are possibly amorphous and therefore not detected by XRD [26].

In this study, a two-stage process that involves pre-polymerization and in situ bulk polymerization was used to yield LDH/PMMA composites. A decrease in the rate of decomposition of the

initiator can appropriately increase the time required to achieve a critical viscosity, corresponding to the pre-polymerization of the MMA [27]. The MMA can then simultaneously facilitate diffusion into the interlayer galleries of the layered material and increase the probability of the polymerization of the MMA with the double bond of the undecenoate anion [28]. The molecular weight of the control PMMA sample obtained by viscosity measurement was $336,600 \pm 8700$.

The XRD patterns of the PMMA/melamine/LDHs are shown along with those of the LDH precursor (Fig. 5). At lower additive loadings (less than 10%), no significant change in the d -spacing is observed for these systems, which may be an indication of the formation of microcomposites and at higher loadings, the LDH peaks disappear, a possible indication of disordering of the LDH layers within the polymer matrix. The melamine peaks are still visible, which indicate that the polymerization does not affect the crystalline structure of melamine. There is, however, no evidence that melamine compatibilizes the LDH and the polymer. In previous work, we have shown that a ZnAl LDH in PMMA is not well-dispersed but instead shows only the presence of tactoids [10]. There is no reason to believe that there is better dispersion in this instance than has been previously seen.

Overall, increasing the melamine loading from 5% to 30% leads to systems with enhanced thermal stability relative to the control PMMA sample. TGA curves of the composites are shifted to higher temperatures as shown in Fig. 6 and the DTG and DTA of the samples are provided in Fig. 7. Kashiwagi et al. identified three steps in the thermal degradation of radically-prepared PMMA, which were assigned to the presence of head-to-head linkages, end-chain unsaturation and the major step was assigned to random scission [29]. With melamine present, for example, the $T_{\max}$ (DTG) of the random scission of the PMMA backbone observed at 373 °C for pure PMMA was shifted to 435 °C for PMMA/30%melamine. The melamine decomposition step (DTG, $T_{\max}$ 361 °C) is not observed in the composites but, as noted in Fig. 6, as the loading of melamine is increased, a mass loss in the temperature range 250–350 °C is observed and this step increases with increasing melamine loading in the samples. Further work must be performed to identify what occurs in this degradation step. The presence of melamine enhances the thermal stability of the composites when 50% mass loss is used as the point of comparison as shown in

Fig. 6. As an example, at 50% mass loss, PMMA/30%melamine shows a 40 °C increment relative to the PMMA control sample.

The thermal stability of the PMMA/LDH systems at both 5% and 10% LDH loadings was also studied and the TGA curves are provided in Fig. 8. The presence of the LDH greatly enhances the thermal stability of the new PMMA composites. Compared with the pure polymer, for example, adding 10% LDH (wt.%) to PMMA leads to improvements of 58° in the onset temperature of degradation and 42° for the midpoint temperature of degradation, which are significant enhancements in the thermal stability of the PMMA/LDH composites.

It was also observed that increasing the LDH loading from 5% to 10% greatly reduces the first step of degradation of PMMA. This can be visualized in the DTA and DTG curves provided in Fig. 9. This behavior is comparable to previous results from this laboratory where carbon nanotubes combined with PMMA also greatly decreased, or suppressed the earlier steps in the degradation of PMMA at this ramp rate (20 °C/min). This effect was attributed to some possible templating effect of CNT during the synthesis of PMMA which may reduce the formation of weak links in the structure [30]. More work needs to be done to fully understand this observation. It should be pointed out that other factors, like the molecular weight of the polymer in a PMMA/LDH or PMMA/melamine system can also play an important role in the properties of the system. Work is underway to elucidate this possibility.

In a review on the use of melamine in the fire retardant market, Crews reported that, based on its decomposition route and its products of decomposition, melamine acts as a heat sink, as well as a blowing agent, and also provides nitrogen-containing gases which presumably dilute the oxygen supply and possibly are chemically involved in the extinguishing process [31]. LDHs may also act as a heat sink since, when heated to higher temperature, they release water molecules that cool the flame. They may also form inorganic protecting layers on the top of the degrading polymer matrix which serve as a barrier to oxygen and heat, thus reducing the fire risks.

The fire properties of different combinations of PMMA, melamine and LDH were evaluated using the cone calorimeter at 50 kW/m². Fig. 10 provides the heat release rate (HRR) curves of PMMA and

PMMA with different loadings of melamine, from 5% to 30%. As observed, there is a gradual decrease in the peak heat release rate (PHRR) with increasing melamine loading. For example, a reduction of 47% is observed with 30% melamine loading and the time to PHRR is increased as more melamine replaces PMMA in the sample, which is also a desirable feature. The summary of all cone calorimetric data is given in Table 1.

The combination of ZnAl LDH with PMMA also performed well in the cone calorimeter. Reductions relative to the pure polymer of 33% and 46%, respectively, for 5% and 10% LDH in PMMA were obtained. The HRR curves of PMMA/ZnAl systems are provided in Fig. 11. These lower loadings of LDH (5–10%) in PMMA give PHRR reductions similar to what is obtained when 30% melamine is used. However, as shown in Fig. 12, the shapes of the HRR curve for these systems are different, with melamine offering a later PHRR relative to the layered double hydroxide. A goal in fire retardancy is to increase the time to ignition and time to PHRR while lowering the PHRR and smoke. As Fig. 12 shows, all systems are equally effective in (slightly) increasing the time to ignition and lowering the PHRR but melamine more effectively increases the time to PHRR.

To study any possible beneficial interaction between ZnAl and melamine in PMMA, different combinations of the two additives were prepared and their fire properties evaluated. The summary of all cone data is provided in Table 1. As shown in this table, in terms of reductions in PHRR, at any particular total additive loading, the reductions are similar, but closer analysis shows that the samples rich in LDH are more efficient at lowering PHRR relative to those containing more melamine. This can be observed in Fig. 13. As shown in this figure, at any particular additive loading (shown by the diagonal), increasing the LDH content increases the reduction in PHRR. The total heat released was not greatly affected by the additives, except at higher melamine loadings, which is probably due to the replacement of some of the polymer by this additive. However, attempts to measure the exact contribution of melamine alone on the THR of the composites were unsuccessful as this additive did not ignite under similar experimental conditions.

The main differences between melamine and zinc aluminum LDH in PMMA are noted in the time to PHRR and the average smoke

produced (ASEA). The LDH shortens the time to PHRR relative to the PMMA/melamine systems at the same total additive loading. Concerning smoke, increasing the melamine content in the polymer reduces the average smoke produced relative to the LDH. There is a good qualitative agreement between the reduction in the mass loss rate and the PHRR, suggesting that the change in PHRR is due to the change in MLR; this has also been observed for MMT nanocomposites [4] and [21].

An unusual aspect of these systems is that the time to ignition is greater in the presence of either or both additives. This is different from the usual observation that the time to ignition is decreased when a nano-dimensional material is added to a polymer. This is a surprising result that requires further investigation.

Some indices have been developed to simplify the interpretation of cone data, including the fire performance index [32], FPI ($\text{s/kW}^{-1}/\text{m}^2$) defined as the ratio of time to ignition to the peak rate of heat release and FIGRA (fire growth rate = $\text{PHRR}/\text{time to PHRR}$) [33]. For a fire retarded polymeric system, the best system will have a longer time to ignition, a longer time to PHRR and a smaller PHRR. From the above definitions of FIGRA and FPI, a higher value for FPI and a smaller one for FIGRA are desired.

As shown in Fig. 14 and Fig. 15, when higher additive loadings are used, all indices show good enhancement in fire properties for the composites. The FIGRA value falls to its minimum, while the % reduction in PHRR and FPI reach their highest values. At any total additive loading level less than 30%, replacing some melamine with the LDH leads to a composite with enhanced fire properties. For example, at 15% total additive loading, comparing PMMA/15%melamine, PMMA/12.5%melamine/2.5%ZnAl and PMMA/10%melamine/5%ZnAl, a gradual increase in the reduction in PHRR is observed (31%, 42%, 48%) and also a gradual increase in FPI (25, 26, 36) while FIGRA goes down slightly. All composites, either melamine alone or with the LDH, are roughly equivalent at 30% loading. The lower (15%) loading sample is expected to have better mechanical properties and is probably the better choice.

Pictures of the residues of some of the selected samples are provided in Fig. 16. Melamine alone does not produce char, and, as the

loading of LDH increases, more char is obtained. As observed in these pictures, the presence of the LDH provides a rather compact inorganic layer, whose mass corresponds to the oxide expected from the LDH loading used. With melamine alone, PMMA burns while boiling (at first a clear liquid) and the boiling liquid transforms to a black layer, which may explain the decrease in the peak HRR observed, but with almost everything consumed by the end of the test. For ZnAl in PMMA, on the other hand, once the sample is ignited, a protecting inorganic/organic layer is noted at an early stage of burning and it solidifies with time. These differences in burning behavior may explain the late time to PHRR noted with PMMA/melamine samples and earlier time to PHRR for PMMA/LDH samples.

The residues collected after the cone experiments were analyzed by XRD for identification. Using XRD and matching different phases with literature PDF cards of known crystalline materials, one can identify the crystalline phases while the amorphous materials must be identified by other means.

Fig. 17 provides the XRD of melamine, and the residues of some selected samples containing both melamine and the LDH. Firstly, it is noted that melamine peaks disappeared after the cone experiment. This was no surprise as melamine alone in PMMA does not leave any residue, as noted in Fig. 16 with residues of PMMA/15%melamine and PMMA/30%melamine. Zinc oxide is the only crystalline material that can be identified by powder diffraction; the peaks due to ZnO are noted on Fig. 17. As also noted in our earlier studies of the char of PMMA/ZnAl prepared by a melt blending process [10], no evidence for aluminum is noted in the cone residue as characterized by XRD. This meant that either aluminum was no longer present in the material or it formed some amorphous phases that could not be distinguished by XRD. When this char is heated to higher temperatures (1000 °C), both ZnO and ZnAl₂O₄ are indexed (not shown here) which means that aluminum is still present in the cone residue in some amorphous phase and heating the char permits the growth of crystals allowing the identification of the aluminum in the newly formed crystalline phases [10].

4. Conclusion

The thermal and fire properties of PMMA modified with both a zinc aluminum undecenoate LDH and/or the commercial fire retardant melamine were studied in this work. The samples were prepared by a two-stage bulk polymerization process and the composites show enhancement in the thermal and fire properties as measured by TGA, DTA, and cone calorimetry. The presence of LDH shows some possible templating effect during the synthesis of PMMA which may reduce the formation of weak links in the structure. While higher loadings of melamine are required to obtain enhancement in fire properties, the LDH seems to give similar reductions in PHRR at lower loading (10%). The effect of the two additives on the fire behavior of the PMMA samples was dictated by type of additive used, with melamine increasing the time to PHRR and lowering the amount of smoke produced relative to the LDH-rich PMMA composites. A sample containing both melamine (10%) and LDH (5%) showed better performance when the reduction in PHRR, FIGRA and FPI were used as the indicators, which shows that there is a benefit to combining these two additives. Composites with 30% total additive loadings also performed well using the 3 indices. The sample with 15% additive is more promising than those containing higher amounts as the mechanical properties are expected to be better at 15%. Compared to the well studied PMMA-layered silicate nanocomposites, both additives show superior fire performances as measured by the cone calorimeter.

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References

1. Ray SS, Okamoto M. Prog Polym Sci 2003;28:1539.
2. (a) Duquesne S, Jama C, Le bras M, Delobel R, Recourt P, Gloaguen JM. Compos Sci Technol 2003;63: 1141;
(b) Bartholmai M, Schartel B. Polym Adv Technol 2004;15:355.
3. Pinnavia TJ, Beall GW. Polymer-clay nanocomposites. New York: Wiley; 2000.

4. Gilman JW, Jackson CL, Morgan AB, Harris R, Manias E, Giannelis EP, et al. Chem Mater 2000;12:1866.
5. Babrauskas V, Peacock RD. Fire Safety J 1992;18:255.
6. Morgan AB. Polym Adv Technol 2006;17:206.
7. (a) Chigwada G, Wilkie CA. Polym Degrad Stab 2003;81:551;
 (b) Jinguo Z, Wilkie CA. Fire and polymers IV. In: ACS symposium series. vol. 922; 2006. p. 61;
 (c) Chigwada G, Jash P, Jiang DD, Wilkie CA. Polym Degrad Stab 2005;89:85.
8. (a) Kandare E, Chigwada G, Wang D, Wilkie CA, Hossenlopp JM. Polym Degrad Stab 2006;91: 1209;
 (b) Kandare E, Hall D, Jiang DD, Hossenlopp JM. Fire and polymers IV: materials and concepts for hazard prevention. In: Wilkie CA, Nelson GL, editors. ACS symposium series. New York: Oxford University Press; 2006;
 (c) Nyambo C, Kandare E, Wilkie CA. PMSE Prepr 2008;98:218.
9. Constantino VRL, Pinnavaia TJ. Inorg Chem 1995;34:883.
10. Manzi-Nshuti C, Hossenlopp JM, Wilkie CA. PMSE Prepr 2008;98:321;
 Manzi-Nshuti C, Wang D, Hossenlopp JM, Wilkie CA. J Mater Chem 2008;18:3091.
11. submitted for publication.
12. Wang LJ, Su S, Wilkie CA. in preparation.
13. Nyambo C, Wang D, Wilkie CA. Polym Adv Tech. in press.
14. Kim S, Wilkie CA. Polym Adv Technol 2008;19:496.
15. Laachachi A, Cochez M, Leroy E, Gaudon P, Ferriol M, Lopez Cuesta JM. Polym Adv Technol 2006;17:327 .
16. Levchik GF, Costa L. Recent Adv Flame Retard Polym Mater 1997;7:64.
17. Williams IG. Plast Rubber Process Appl 1984;4:239.
18. Shimasaki C, Watanabe N, Fukushima K, Rengakuji S, Nakamura Y, Ono S. et al. Polym Degrad Stab 1997;58:171.
19. Reshetnikov I, Antonov A, Rudakova T, Aleksjuk G, Khalturinskij N, Polym Degrad Stab 1996;54:137.

20. Kurata M, Tsunashima Y. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley; 1999. p. VII. 1-83.
21. Gilman JW, Kashiwagi T, Nyden M, Brown JET, Jackson CL, Lomakin S. et al. In: AI-Malaika S, Golovoy A, Wilkie CA. editors. Chemistry and technology of polymer additives. Oxford: Blackwell Scientific; 1999. p. 249-65.
22. Borja M, Dutta PK. J Phys Chem 1992;96:5434.
23. Xu ZP, Braterman PS, Yu K, Xu H, Wang Y, Brinker CJ. Chem Mater 2004;16:2750-6.
24. Klopogge JT, Frost RL. J Solid State Chem 1999;146:506.
25. Xu ZP, Braterman PS, Seifollah N. In: Abstract in proceedings of the 224th ACS national meeting. 18-22 August 2002, Boston, MA. p. Coll. 219.
26. Kooli F, Chisem IC, Vucelic M, Jones W. Chem Mater 1996;8:1969.
27. Avella M, Errico ME, Martuscelli E. Nano Lett 2001;1:213.
28. Wang G-A, Wang C-C, Chen C-Y. Polymer 2005;46:5065.
29. Kashiwagi T, Inaba A, Brown Ej. Macromolecules 1986;19:2160.
30. Costache MC, Wang D, Heidecker MJ, Manias E, Wilkie CA. Polym Adv Technol 2006;17:272.
31. Crews GM. Fire retardant chemicals association (US). Technical and marketing issues impacting the fire safety of building and construction and home furnishings applications. Paper presented at the 1992 spring conference. Orlando, FL.
32. Zanetti M, Camino G, Cavanese D, Morgan AB, Lamelas FJ, Wilkie CA. Chem Mater 2002;14:189.
33. Schartel B, Hull TR. Fire Mater 2007;31 :327.

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Appendix

Table 1 Cone summary results of PMMA and melamine and ZnAI systems at 50 kW/m²

Formulation	PHRR (kW/m ²) (% reduction)	t _{PHRR} (s)	THR (MJ/m ²)	ASEA (m ² /kg)	AMLR (g/s m ²) (% reduction)	T _{ign} (s)
PMMA	1024 ± 73 (NA)	103 ± 5	78 ± 1	124 ± 2	30.7 ± 1.2 (NA)	9 ± 1.2
PMMA 95:Mel 5:ZnAI 0	761 ± 46 (26)	122 ± 6	76 ± 1	156 ± 9	24.6 ± 0.5 (20)	17 ± 2.8
PMMA 92.5:Mel 7.5:ZnAI 0	834 ± 55 (19)	124 ± 9	74 ± 2	140 ± 9	26.0 ± 1.5 (15)	16 ± 0.5
PMMA 90:Mel 10:ZnAI 0	762 ± 80 (26)	137 ± 8	74 ± 1	141 ± 7	24.5 ± 1.8 (20)	17 ± 0.7
PMMA 85:Mel 15:ZnAI 0	703 ± 63 (31)	126 ± 8	74 ± 0	145 ± 9	23.5 ± 1.6 (23)	17 ± 3.0
PMMA 70:Mel 30:ZnAI 0	541 ± 36 (47)	126 ± 10	69 ± 1	112 ± 17	19.2 ± 1.0 (39)	22 ± 1.2
PMMA 95:Mel 0:ZnAI 5	689 ± 62 (33)	102 ± 11	74 ± 2	209 ± 33	22.4 ± 1.4 (27)	21 ± 1.2
PMMA 90:Mel 0:ZnAI 10	558 ± 56 (46)	96 ± 7	71 ± 1	287 ± 14	18.1 ± 2.3 (41)	21 ± 1.0
PMMA 95:Mel 2.5:ZnAI 2.5	704 ± 47 (31)	125 ± 16	77 ± 1	163 ± 3	23.5 ± 0.8 (23)	16 ± 0.4
PMMA 90:Mel 2.5:ZnAI 7.5	553 ± 42 (48)	106 ± 25	72 ± 1	229 ± 29	18.6 ± 1.0 (39)	18 ± 2.4
PMMA 90:Mel 5:ZnAI 5	559 ± 37 (45)	100 ± 5	72 ± 1	206 ± 7	19.5 ± 1.2 (36)	17 ± 2.3
PMMA 90:Mel 7.5:ZnAI 2.5	633 ± 56 (38)	114 ± 11	74 ± 1	196 ± 24	21.5 ± 1.3 (30)	18 ± 4.6
PMMA 85:Mel 12.5:ZnAI 2.5	599 ± 51 (42)	114 ± 11	71 ± 0	202 ± 11	20.7 ± 1.3 (33)	15 ± 2.3
PMMA 85:Mel 10:ZnAI 5	536 ± 10 (48)	123 ± 19	69 ± 1	204 ± 17	19.1 ± 0.1 (35)	19 ± 2.7
PMMA 70:Mel 27.5:ZnAI 2.5	491 ± 42 (52)	118 ± 1	67 ± 0	162 ± 15	18.1 ± 0.9 (41)	15 ± 1.9
PMMA 70:Mel 25:ZnAI 5	512 ± 16 (50)	127 ± 11	66 ± 1	161 ± 5	18.7 ± 0.5 (36)	18 ± 1.3

Figure 1 XRD traces of Zn3Al undecenoate LDH (ZnAI) used in this work.

Figure 2

FT-IR of ZnAl undecenoate LDH (KBr pellet). (a) -OH group; (b) C-H stretching vibration for sp^2 carbon of undecenoate anion; (c) C-H stretching vibration for sp^3 carbon of undecenoate anion; (d) C=C stretching vibration for the sp^2 carbon of the 10-undecenoate anion (e) H-bonded acid; (f) asymmetric stretch of $RCOO^-$; (g) symmetric stretch of $RCOO^-$; (h) scissoring bending vibration of C-H in plane bonds; (e) the two strong bands are out-of-plane bending vibrations of C-H, which bond to the 10-undecenoate.

Figure 3

TGA and its derivatized mass, DTG of ZnAl LDH in a nitrogen environment (50-800 °C). (Note: TGA shows about 4% mass loss at 150 °C, which correlates well with the predicted water loss (4%) based on H₂O unit shown in formula from elemental analysis.)

Figure 4

DTA of ZnAl LDH in a nitrogen environment. at 20 °C/min, from 50 to 800 °C.

Figure 5

XRD traces of selected PMMA/melamine/LDH samples (P: PMMA; Me: melamine; ZnAl: Zn3Al undecenoate LDH; digit (2.5-90: % loading)).

Figure 6

TGA of melamine and PMMA with different loadings of melamine. (A) Melamine; (B) PMMA; (C) PMMA/5%melamine; (D) PMMA/7.5%melamine; (E) PMMA/ 10%melamine; (F) PMMA/15%melamine; (G) PMMA/30%melamine. The TGAs were run in a nitrogen environment at 20 °C/min from 100 to 800 °C.

Figure 7

(I) DTA and (II) DTG of PMMA/melamine composites (nitrogen environment, 20 °C/min). (A) Melamine; (B) PMMA; (C) PMMA/5%melamine; (D) PMMA/7.5%melamine; (E) PMMA/10%melamine; (F) PMMA/15%melamine; (G) PMMA/30%melamine.

Figure 8

TGA curves of PMMA/LDH composites, run in a nitrogen environment, from 100 to 600 °C at 20 °C/min. (A) PMMA; (B) PMMA/5%ZnAl; (C) PMMA/10%ZnAl.

Figure 9

(I) DTA and (II) DTG curves of PMMA/LDH composites, run in a nitrogen environment, from 100 to 600 °C at 20 °C/min. (A) PMMA; (B) PMMA/5%ZnAl; (C) PMMA/10%ZnAl.

Figure 10

HRR curves of PMMA/melamine systems at 50 kW/m². (A) PMMA; (B) PMMA/5%melamine; (C) PMMA/7.5%melamine; (D) PMMA/10%melamine; (E) PMMA/15%melamine; (F) PMMA/30%melamine.

Figure 11

HRR curves of PMMA/LDH systems at 50 kW/m². (A) PMMA; (B) PMMA/5%LDH; (C) PMMA/10%LDH.

Figure 12

HRR curves of PMMA and selected PMMA/LDH and melamine combinations at 50 kW/m². (A) PMMA; (B) PMMA/10%melamine; (C) PMMA/10%ZnAl; (D) PMMA/30%melamine.

Figure 13

The reduction in PHRR of the different composites plotted against the % melamine and % LDH loadings. (Note: the diagonal on this plot represents a given total additive loading.)

Figure 14

Reduction in PHRR, time to ignition (t_{ign}), fire performance indexes (FPI) and fire growth rate (FIGRA) of different PMMA and ZnAI and melamine compositions (P = PMMA; M = melamine; LDH = Zn3Al undecenoate).

Figure 15

3D plots of different indexes vs melamine and LDH loadings: (A) FPI vs % melamine vs % LDH and (B) FIGRA vs % melamine vs % LDH. (Note: in both plots, the diagonal represents a particular constant additive loading.)

Figure 16

Pictures of some of the cone residues of PMMA/melamine/ZnAI after cone experiment. (Note: (a) background; (b) aluminum foil; (c) char residue.)

Figure 17

XRD traces of the char residue after cone experiment of selected PMMA/melamine/LDH samples (P: PMMA; Me: melamine; ZnAI: Zn3AI undecenoate LDH; digit (2.5-90: % loading)).