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# Comparative Study on the Flammability of Polyethylene Modified with Commercial Fire Retardants and a Zinc Aluminum Oleate Layered Double Hydroxide

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## **Abstract:**

Polyethylene (PE) was modified by the addition of a layered double hydroxide of zinc aluminum oleate (ZnAl) and/or commercial fire retardants.

Commercial additives included: melamine polyphosphate (MPP), ammonium polyphosphate (APP), triphenol phosphate (TPP), resorcinol diphosphate (RDP), decabromophenyl oxide (DECA) and antimony oxide (AO). The thermal stability and the combustion behaviors of the new composite polymeric materials are evaluated in TGA experiments and cone calorimetry. At 20% total additive loading, APP and LDH enhance the thermal stability of the PE composites and favor char formation. ZnAl leads to the best reduction in the peak of heat release rate (PHRR), 72%, while the combinations of PE with other additives give reductions in the range 20–40%. The combination of DECA and AO effectively increases the time to ignition and time to PHRR while LDH lowers these two parameters. APP and MPP on the other hand, do not affect the time to ignition, but they effectively increase the time to PHRR relative to the pristine polymer.

## 1. Introduction

The demand for cost-effective structural materials with enhanced properties has led to a rapid proliferation of high-performance and specialty polymers in the building construction, automotive and aerospace industries. The extreme variability in chemical composition which characterizes this class of materials has created a pressing need for new and better treatments for reducing flammability [1]. The additives that are used are mainly halogenated [2], but also non-halogenated additives have been effective in lowering both the peak of heat release rate and the total heat released, however the time to ignition is not changed compared to the virgin polymer [3], 3a, 3b and 3c.

Recent studies on the flammability of polymers have focused on layered inorganic compounds because these materials possess unique properties as fillers in polymeric nanocomposites. These nanomaterials can be, in fact, exfoliated into single layers, each of them having thickness of the order of 1 nm, and the surface of the layers may be functionalized by ion exchange or grafting reactions with organic groups that increase the compatibility with the polymers [4]. In addition, layered solids may intercalate polymeric chains into their interlayer regions [5]. The nanocomposites then formed exhibit improved performance compared with virgin polymers: improved flexural modulus, increased heat distortion temperature (HDT), decreased permeability and improved fire properties.

Nanocomposite formation using layered silicates have been shown to significantly decrease the flammability of the resulting polymers. A series of nanocomposites based on polymerically modified clays at 5% inorganic clay loading have been prepared and investigated: PS/COPS clay nanocomposite achieved a 57% reduction in PHRR, while PE/triclay achieved a 60% reduction [6]. 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 [7]. Synergy using the oxygen consumption cone calorimetry was also reported between the nanocomposites of polypropylene-graft-maleic anhydride and conventional vapor phase fire retardants, such as the combination of decabromodiphenyl oxide and antimony oxide [8]. Recently, Faghihi and coworkers reported that the flame retardant compounds containing talc, such as PP/APP/EVA/PA-6/talc, showed an increase in the residual weight and flame retardant properties after ignition and the formation of a ceramic-like protective layer on the surface of the carbon-rich char which increased the LOI to more than 30 vol% [9].

Most of these studies on the fire retardancy of polymer nanocomposites have focused on the use of layered silicate systems while the layered double hydroxide (LDH) systems have been much less reported in the literature [10], 10a, 10b, 10c and 10d. The LDHs can be represented by the ideal formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{m-}_{x/m} \cdot nH_2O]$ , where  $M^{II}$  and  $M^{III}$  are divalent and trivalent metal cations, such as  $Mg^{2+}$ ,  $Al^{3+}$ , respectively, A is an anion of charge  $m$  such as  $NO_3^-$ ,  $CO_3^{2-}$ , and  $C_{12}H_{25}SO_4^-$ . LDHs are important layered crystals due to their wide applications as catalysts, flame retardants, stabilizers, medical materials, etc. [11]. These LDH nanomaterials were recently found to be particularly effective fire retardants for polar polymers like poly(methyl methacrylate) rather than non-polar polystyrene [12]; the performance of LDHs in PMMA was found to be comparable with that of the layered silicates when evaluated by the reduction in PHRR [12] and [13]. It was also observed that the identity of the divalent or trivalent metal cation [13] and the anion chain length [14] does play a role in the amount of reduction obtained. With the cationic clays [15], there is a very close connection between dispersion and reduction in PHRR, but this is not seen with LDHs. Even poorly dispersed LDHs can give a significant reduction in the PHRR.

Recently, synergistic effects were observed in both TGA and cone calorimetry for formulations containing both MgAl undecenoate LDH and APP in polystyrene [16]. The observed thermal stability and fire performance were thought to be due to physical and chemical interactions between MgAl-LDH, APP and the polymer. A combination of melamine and a ZnAl undecenoate LDH in PMMA has also been investigated [17]; both melamine and LDH were found to be effective alone with PMMA, but a sample containing both melamine (10%) and LDH (5%) showed better performance when the reduction in PHRR, FIGRA and FPI were used as the indicator, which showed that there is a benefit to combining these two additives.

A few examples also exist where LDHs are found to be effective with non-polar polymers. The dispersion of a low loading (ca. 5%) of zinc aluminum stearate LDH was reported to give a 55% reduction in heat release rate during combustion of PE. In our recent studies on the combustion of PE, we also noted that a zinc aluminum LDH modified with oleate anions leads to a 58% reduction in PHRR at 10% loading (wt.%) but modest reductions are obtained when a magnesium aluminum oleate LDH is used. These results confirm that it is possible to render LDH compatible with non-polar polymer by careful choice of the metals and the charge balancing anions.

The work presented in this publication is part of an ongoing investigation where the goal is to design new formulations of fire retardants for non-polar polymers. The effectiveness of several combinations of commercial fire retardants, like phosphates (RDP, TPP, APP), melamine based fire retardants (MPP), and halogenated fire retardants (decabromophenyl oxide with or without antimony oxide) and a layered nanomaterial, zinc aluminum LDH, are investigated. This study uses the cone calorimeter as the evaluating tool, but the selected fire retardants may also enable these PE systems to pass other regulatory tests (e.g. UL 94 protocol).

## 2. Experimental section

### 2.1. Materials

Zinc nitrate hexahydrate (98%) and sodium hydroxide, extra pure pellets, were purchased from Aldrich Chemical Co. Sodium oleate (powder, purified) was obtained from J.T. Baker. Low-density polyethylene (PE) Petrothene NA960000, was supplied by Equistar Chemicals Co. The commercial fire retardant used in this work are listed in Table 1.

The oleate-containing LDH was synthesized adopting the co-precipitation method [18]. This method requires the addition of an  $M^{II}/M^{III}$  metal salt solution to a basic solution of the desired anions 19a, 19b and [19]. The synthesis of ZnAl oleate has been previously fully described [20].

The PE composites were prepared in a Brabender Plasticorder at high speed (60 rpm) at 140 °C. The residence time in the Brabender mixer was 10 min for all composites. The composition of each sample is calculated from the amount (wt.%) of layered double hydroxide and/or commercial fire retardant and polymer charged to the Brabender.

Fourier transform infrared (FT-IR) spectra of the solid materials were obtained on a Nicolet Magna-IR 560 spectrometer in the 650–4000  $\text{cm}^{-1}$  region (ATR mode). Powder X-ray diffraction measurements (XRD) were performed in a Rigaku Miniflex II Desktop X-ray diffractometer. Data acquisition was performed using a scan speed of 2.00°/min, at a sampling width of 0.020° from 2.00 to 40.00 ( $2\theta$ ). Elemental analysis was carried out by Huffman Labs, Colorado, using atomic emission spectroscopy interfaced with inductively coupled plasma (AES-ICP) for metal determination. The thermal stability of the samples is studied by thermogravimetric analysis on a TG 209 F1 under air atmosphere (40  $\text{ml min}^{-1}$  flow rate) at 20 °C/min. The experiments were run in triple and averages are reported.

### 2.2. Combustion

Cone calorimeter measurements were performed on an Atlas CONE-2 according to ASTM E 1352 at an incident flux of 50  $\text{kW/m}^2$ ,

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  $3 \times 100 \times 100 \text{ mm}^3$  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

#### 3.1. Characterization of oleate LDH

The composition of the LDH was calculated from elemental analysis as  $\text{Zn}_{2.49}\text{Al}_{1.00}(\text{OH})_{6.98}(\text{Oleate})_{1.00} \cdot 2.02\text{H}_2\text{O}$ . The water content (5.1%) was estimated by TGA experiment (air, 20 °C/min, 50–800 °C). The FT-IR spectra of ZnAl is given in Fig. 1 and shows common IR bands characteristic of long-chain carboxylate LDH compounds [19], 19a and 19b: a broad band at  $\sim 3500 \text{ cm}^{-1}$  ( $\nu_{\text{OH}}$  of layer hydroxide), the asymmetric and symmetric  $\nu_{\text{CH}}$  at  $3000\text{--}2800 \text{ cm}^{-1}$  and two strong bands at  $1600\text{--}1400 \text{ cm}^{-1}$  (asymmetric and symmetric carboxylate bands). There is also a distinctive feature: a weak peak at  $3006 \text{ cm}^{-1}$  associated with  $\nu_{\text{CH}}$  attached to a double bond [22]. All the above peaks confirm the presence of the oleate carboxylate chain.

Fig. 2 shows the XRD traces of ZnAl. This material is well layered as both the second and third reflections are visible, indicating long range ordering in the *c*-direction. The *d*-spacing of ZnAl is found to be 3.96 nm [the average interlayer spacing was estimated as  $d_{003} + 2d_{006} + \dots + nd_{00(3n)}/n$ ]. Oleate requires a packing mode different from extended  $\text{C}_{18}$  anions [23], 23a and 23b because its *cis* geometry imposes a bend in the middle of the chain. This bend allows the chains to overlap only in the region below the double bond. The bending geometry of oleate in the LDH interlayer is similar to the boomerang shape that oleic acid employs in its crystallization [24]. Like the stearate anions, these long organophilic anions are expected to render the LDH more compatible with polymers.

The morphology of the PE systems containing fire retardants was assessed by XRD, as shown in Fig. 3 and Fig. 4. The addition of 20% ZnAl to PE leads to smaller shift of the LDH diffraction peaks to lower  $2\theta$  values, suggesting intercalation if one only consider the 2nd

and 3rd diffraction peaks of the XRD trace of the PE/20%ZnAl system; the first reflection should appear at  $2\theta < 2$ , which is below the instrument set limit. The diffraction peaks are however broad and asymmetric, which means that the intercalation of the polymer between the layers of the LDH causes disordering of the layers and also reduces the number of stacked layers. The increment in the basal spacing observed for the PE/20%ZnAl system may also be due to the dehydration and reorientation of anions between the layers after the melt blending process.

It should be pointed out that the  $d$ -spacing of this LDH (3.96 nm) is large enough for this material to accommodate some polymeric chains without noticeable change in interlayer spacings, making assumptions about the anion packing. In other experiments, the TEM images of PE composites in the presence of only 3% ZnAl revealed homogenous dispersion, and these images were better than the ones of PE modified with a magnesium aluminum oleate LDH at a similar loading (i.e. finer LDH-dispersion or composite-structure for ZnAl than for MgAl) [20]. The higher additive loadings studied in this work (10–20 wt.%) however minimize the possibility of nanocomposite formation for the melt blended PE/fire retardant systems.

The combination of ZnAl, DECA and AO shows similar XRD patterns as PE/ZnAl, also suggesting intercalation with disordering (Fig. 3). DECA and AO in PE do not lead to any diffraction peak, which is expected as these fire retardant additives are not layered. It is worth mentioning that combining ZnAl (10%) with APP, TPP and MPP led to the disappearance of the diffraction peaks, suggesting exfoliation or disordering of the LDH in the polymer matrix (Fig. 4). However, at 20% additive loading, disordered systems are more likely.

### *3.2. Flammability*

The burning of polymeric material may be viewed as a two-step process whereby volatile fragments produced in the thermal degradation of the condensed phase mix with the ambient oxygen in the gas phase where they are combusted [25], 25a and 25b. Then, the activity of fire retardants is due to their ability to inhibit free-radical reactions which propagate gas-phase combustion and/or to their capacity to depress the rate of evolution of volatile compounds from the condensed phase [26], 26a, 26b and 26c.



The heat release rate curves of the PE/LDH systems are shown in Fig. 5. For a fire retarded polymeric system, the best system should have a longer time to ignition, a longer time to PHRR and a smaller PHRR. When the LDH is present, the PHRR is greatly lowered; the reduction in PHRR is 58% at 10% LDH loading while 20% loading increases the reduction to 72%. The time to ignition is decreased as more LDH is added to PE. Just after ignition, the heat release rate curves of PE/LDH systems increase much more quickly than in the pristine polymer and a compact carbonaceous layer which is a mixture of metal oxide and/or spinel [13] and [20] is quickly formed on the surface of the polymeric sample. This mixture of metal oxides resulting from the decomposition of the LDH effectively protects the polymer from heat and explains for example the plateau observed in the HRR curves of these composites at both 10 and 20% loadings. The early time to peak heat release rate of the LDH composites is possibly due to the thermal decomposition of the oleate anions, resulting in the formation of volatile combustibles at an early stage of burning. The general observation with almost all nanocomposites is that the time to ignition is decreased; this is an ongoing matter for discussion.

The comparability between the reductions in both PHRR and AMLR as shown in Table 2, reveals that the mode of action of an LDH and a layered silicate may be the same. For MMT/modified polymer nanocomposites, the reduction in PHRR has been explained by a chemical and physical action of the inorganic layers dispersed in the polymer matrix [8] and [27].

Adding MPP to the PE system decreases the PHRR relative to the pristine polymer, as shown in Fig. 6. Reductions of 25% and 26% are noted for PE/10%MPP and PE/20%MPP, respectively. These numbers are quite similar, even though the loading doubles, which clearly shows that MPP is not very effective at lowering the PHRR of PE. The addition of MPP, however, does not affect the time to ignition of the composites, and effectively increases the time to PHRR, with 20% MPP being superior to 10% MPP and the pure polymer. For example, the HRR curve of the pristine polymer peaks at 116 s, but 10% MPP pushes the tPHRR to 145 s while 20% MPP increases this to 166 s. PE/10%ZnAl 10%MPP (curve D) ignites earlier than the pure polymer and gives a 56% reduction in PHRR. This system does not reach the 72% reduction obtained with PE/20%ZnAl, and in fact, is quite similar

to 10% ZnAl, i.e., the addition of melamine does not offer improved fire performance.

The addition of ammonium polyphosphate (APP) to PE gives results similar to those with MPP as shown in Fig. 7; the time to ignition is not affected by replacing 10% or 20% polymer with APP and also, this additive increases the time to PHRR relative to the pristine polymer. Unlike MPP, where both 10 and 20% loading in PE result in comparable reductions in PHRR, 20% APP gives a 35% reduction in PHRR while 10% of this additive is ineffective. This type of behavior is currently being investigated in these laboratories as it is observed that the reduction in PHRR is not always proportional to the amount of additives used. It is likely that this parameter is related to both the polymer type and the additive used. It is certain that the type of dispersion will also have an effect on the fire properties. One cannot rule out other factors like the preparative mode of the composites or the selected heat flux in the cone experiment. The combination of 10% APP and 10% ZnAl leads to a 43% reduction in PHRR, a lower reduction than seen for 10% ZnAl alone and thus the combination does not offer an advantage.

It is well known that the combination of DECA and AO is an effective fire retardant system for non-polar polymers [28]. Fig. 8 gives the HRR curves of PE modified with AO, DECA and ZnAl. At 20% total additive loading, the combination of DECA and AO is ineffective at lowering the PHRR of the composite. Interestingly, PE/16%DECA 4%AO ignites after 54 s, which is 16 s later than that of the pristine polymer. The time to PHRR is also increased from 116 s for PE to 137 s. Adding 10% ZnAl to the PE/8%DECA 2%AO system results in only a 24% reduction in PHRR, half the reduction obtained when only 10% ZnAl is used. Once again, there is no advantage to this combination.

Zanetti et al. reported a synergistic effect when PP-g-MA is modified with DECA, AO and an organically modified silicate clay [8]. The nanocomposites of PP-g-MA/layered silicate showed a lower PHRR relative to the pristine material, but the peak heat release rate was reduced still further when antimony oxide or decabromophenyl oxide was present. When both additives were present, a synergistic effect, which did not occur under identical testing conditions when antimony oxide and the brominated fire retardant were added to the control PP-

g-MA polymer, resulted. Their conclusions contrast the current results where no beneficial interaction is observed when PE/LDH system is combined with DECA and AO. The main differences between the two studies are the polymers, PE versus PP, and the compatibilizer, maleic anhydride. The role of the compatibilizer on the fire properties of non-polar polymers modified with these new anionic clays is currently under investigation.

The phosphorus containing additives, RDP and TPP, at 20% loading, lead to a 34% and a 24% reduction in PHRR, respectively. The combination of ZnAl with either phosphate in PE shows an antagonistic effect as observed in Table 2 where reductions of less than 20% are recorded. A compatibility issue, shown by a poor mixing of the phosphate in the polymer is observed while preparing the composites in the brabender mixer. While adding the LDH to the PE/RDP or PE/TPP system apparently helps in the melt blending process, the lower reductions in PHRR noted for the PE/LDH/phosphate-FR relative to the PE/phosphate-FR systems may be an indication that at a nanolevel, good mixing is still not achieved. This observation is supported by XRDs where the combinations of LDH and fire retardant (FR) in PE does not show any diffraction peak, a probable sign of formation of disordered systems.

These results contrast previous work where PS modified with a magnesium aluminum undecenoate combined with APP gave large reductions in PHRR relative to the pristine PS [16]. Similarly, the combination of melamine and a zinc aluminum undecenoate was found to be effective for the polar poly(methyl methacrylate); a sample containing both melamine (10%) and LDH (5%) showed better performance when the reduction in PHRR, FIGRA and FPI was used as the indicator [17]. The results presented in this work reveal no synergy between the selected commercial fire retardant and the non-polar PE. The amount of the reduction in PHRR (72%) found for PE/20%ZnAl is superior to previous results and raises the question of whether even higher reduction can be achieved with the use of more ZnAl; more work still needs to be done to understand all factors that are more important when using an LDH as fire retardant additive for polymers.

This work raises the question of the generality of nano-dimensional materials used together with conventional fire retardants.

The systems that has been investigated, MMT with bromine [8], with phosphorus [29], and with mineral plus LDH with APP [16] and melamine [17], have been seen to be effective but the ZnAl LDH shows no positive interactions with conventional fire retardants in PE. Further work will be necessary to determine the cause of this behavior.

### 3.3. Char formation

Under normal circumstances, polyethylene does not char when it is burned. Rather, its thermal degradation is dominated by random scission of the C–C bonds followed by hydrogen transfer and disproportionation. These reactions produce a broad distribution of volatile hydrocarbons [30]. The protection offered by the LDH to the polymer is shown by the reduction in PHRR and it is explained by the formation of a layer of metal oxides on the polymer surface when the sample is subjected to heat. Char formation is good for fire retardancy purposes as the char prevents the entry of flammable gases into the gas phase and insulates the underlying polymer from the flame [31].

As shown in Fig. 9, both LDH and APP effectively enhance char formation while the other additives are less effective. At 20% total additive loading, the PE/APP sample gives 12% of the original sample as char, followed by the LDH (8%). DECA, RDP, TPP and MPP do not favor char formation. The char morphology appears to be very important when comparing LDH and APP. As noted in Fig. 9, the char of PE/20%LDH covers all the surface of the aluminum foil. PE/20%APP leaves heavier char as mentioned above, but shows cracks which possibly explain lower reduction in PHRR recorded for the PE/20%APP sample relative to the LDH-rich sample. The interesting result is observed when one compares the action of APP and MPP in the presence of ZnAl; PE/20%MPP leaves a negligible amount of char (<2%) while PE/20%APP gives a heavier (12%) and more dense char. But, when 10% APP or 10% MPP are combined with ZnAl (10%), a more compact char, but lighter (4% by weight) is noted for PE/10%ZnAl 10%MPP relative to the PE/10%ZnAl 10%APP system (12% by weight). PE/10%ZnAl 10%MPP also gives a larger reduction in PHRR (56%) relative to PE/10%ZnAl 10%APP (43%). The contrast between the morphology of the cone residues of the two samples suggests that there is a good correlation between the char morphology rather than the mass of the residue and the reduction in PHRR of the composites.

### 3.4. Thermal stability

In Fig. 10, the thermo-oxidative behavior of PE is compared with PE modified with ZnAl and/or APP. As noted in this figure, PE degrades in a single step and does not leave any char at 600 °C. The presence of either LDH or APP enhances the thermal stability of the composites and increases the char formed at 600 °C, as also noted in the summary in Table 3. MPP on the other hand decreases the thermal stability of PE and does not yield any char residue. When MPP is combined with ZnAl, a new system more thermally stable than that containing only MPP is obtained (Fig. 11). The presence of the LDH produces a barrier effect to oxygen diffusion into the heated polymer due to the accumulation of the oxides on the surface of the polymer [32]. As was noted earlier in the analysis of the cone residues, APP also enhances char formation relative to MPP in TGA experiments.

## 4. Conclusions

The presence of 10 or 20% ZnAl LDH enhances the thermal stability and the fire properties of PE. The best reduction in PHRR (72%) is recorded for PE/20%ZnAl, but this system ignites quickly relative to the pristine PE sample. The combination of phosphate-containing fire retardant (APP, MPP) with PE does not affect the ignition time while DECA and AO increase the time to ignition of these PE composites. The commercial fire retardants, in general, increase the time to PHRR relative to the pristine sample and the reduction in PHRR range between 20 and 40% at 20% total additive loadings. LDH and APP favor char formation and function in the condensed phase while the combination of DECA and AO is vapor phase active. The combination of these conventional fire retardants with the ZnAl LDH does not offer any advantage in PHRR reductions and, in fact, gives a lower reduction, but some of these do effectively increase the time to ignition and/or the time to PHRR.

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## Appendix

**Table 1** Commercial fire retardants and their sources

Fire retardant	Source
Antimony oxide (AO)	Laurel Industries, Inc.
Decabromophenyloxiide (DECA)	Albemarle Corporation
Melamine polyphosphate (MPP)	CIBA Speciality Chemicals
PHOS-CHEK (APP)	ICL-Performance Products LP
Fyrolflex RDP (RDP)	Supresta
Triphenyl phosphate (TPP)	Akzo Nobel

Note: in parentheses, the nomenclature adopted for the purpose of this work is provided.



**Table 2** Cone summary results of PE modified with different fire retardants (50 kW/m<sup>2</sup>).

Formulation	PHRR	(% red.)	tPHRR	THR	AMLR	VOS	t <sub>ign</sub>
PE	1888 ± 288	NA	116 ± 5	148 ± 21	27.0 ± 2.0	908 ± 106	38 ± 4.0
PE/10%ZnAl	796 ± 65	58	154 ± 18	118 ± 2	16.1 ± 1.3	1679 ± 95	19 ± 5.9
PE/20%ZnAl	520 ± 38	72	77 ± 27	116 ± 4	10.8 ± 1.8	1928 ± 21	18 ± 0.9
PE/10%APP	1965 ± 97	4	126 ± 2	123 ± 2	26.9 ± 0.5	1146 ± 100	28 ± 6.0
PE/20%APP	1226 ± 46	35	145 ± 13	110 ± 3	19.5 ± 1.6	1375 ± 70	31 ± 5.1
PE/10%MeIapur	1425 ± 369	25	145 ± 19	125 ± 1	21.6 ± 1.9	1009 ± 14	23 ± 2.5
PE/20%MeIapur	1400 ± 208	26	166 ± 17	135 ± 9	21.6 ± 0.6	887 ± 49	26 ± 2.2
PE/10%ZnAl 10%APP	1077 ± 49	43	100 ± 15	128 ± 6	18.9 ± 1.4	1224 ± 46	17 ± 0.6
PE/10%ZnAl 10%MeIapur	835 ± 81	56	65 ± 3	127 ± 5	14.9 ± 1.7	1412 ± 80	14 ± 1.0
PE/10%RDP	1391 ± 194	26	111 ± 12	122 ± 3	20.0 ± 5.2	1300 ± 121	41 ± 8.6
PE/20%RDP	1249 ± 81	34	105 ± 6	108 ± 18	20.5 ± 6.4	1385 ± 252	23 ± 12.3
PE/10%TPP	1795 ± 322	5	120 ± 22	135 ± 17	21.8 ± 3.3	1307 ± 331	41 ± 2.2
PE/20%TPP	1434 ± 119	24	138 ± 14	122 ± 6	21.6 ± 1.8	1715 ± 90	35 ± 9.9
PE/10%ZnAl 10%RDP	1626 ± 54	14	120 ± 6	124 ± 3	22.3 ± 4.7	1246 ± 57	22 ± 1.4
PE/10%ZnAl 10%TPP	1736 ± 174	8	120 ± 14	138 ± 7	24.3 ± 1.7	1389 ± 78	26 ± 2.1
PE/20%DECA	1724 ± 324	9	137 ± 10	109 ± 7	29.9 ± 8.2	2472 ± 114	47 ± 7.2
PE/16%DECA 4%AO	1946 ± 339	3	137 ± 11	89 ± 5	28.5 ± 8.4	2128 ± 789	54 ± 2.1
PE/10%ZnAl 8%DECA 2%AO	1431 ± 121	24	93 ± 5	122 ± 7	25.3 ± 2.2	2482 ± 232	20 ± 1.7

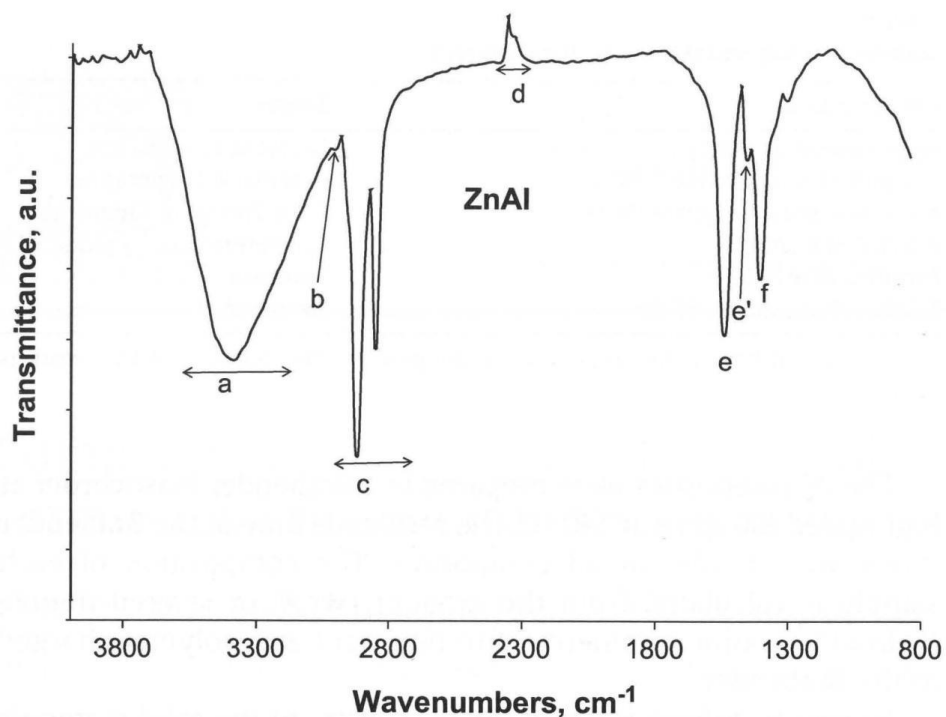
Note: PHRR (kW/m<sup>2</sup>) is the peak of heat release rate; (% red.) is the % reduction relative to the control sample; tPHRR (s) is the time to PHRR; THR (MJ/m<sup>2</sup>) is the total heat released; AMLR (g/s m<sup>2</sup>); VOS (l) is the volume of smoke; t<sub>ign</sub> (s) is the time to ignition.

**Table 3** TGA summary results of PE modified with ZnAl, APP and MPP.

Formulation	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	% Char
PE	365	408	0
PE/20%ZnAl	397	449	8
PE/20%MPP	339	388	0
PE/10%ZnAl 10%Melapur	371	439	4
PE/20%APP	368	454	16
PE/10%ZnAl 10%APP	371	462	13

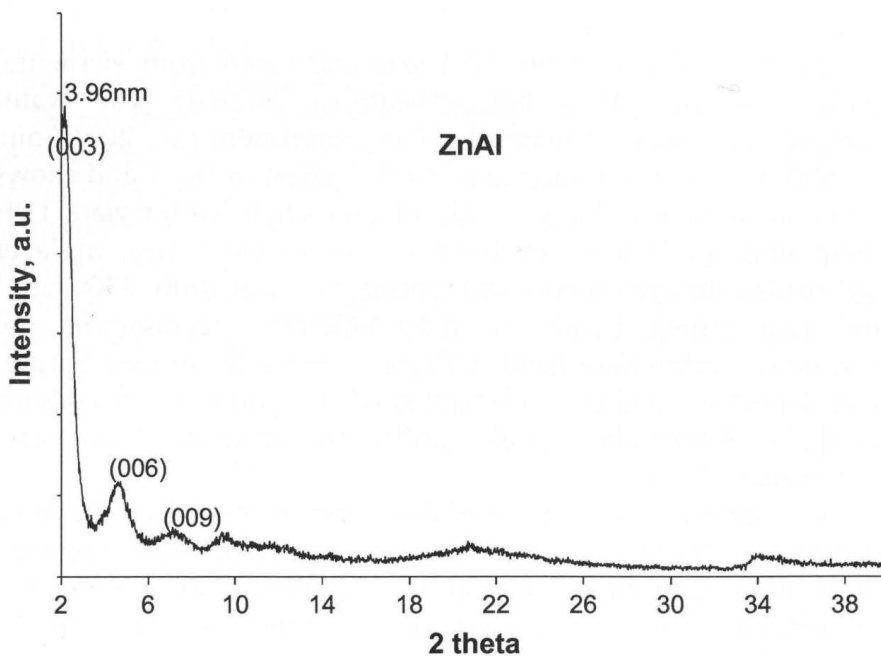
Note: the TGA results are an average of 3 determinations.  $T_{0.1}$  is the onset temperature of degradation (temperature at 10% mass loss) and  $T_{0.5}$  is the temperature at 50% mass loss (°C).

**Figure 1**



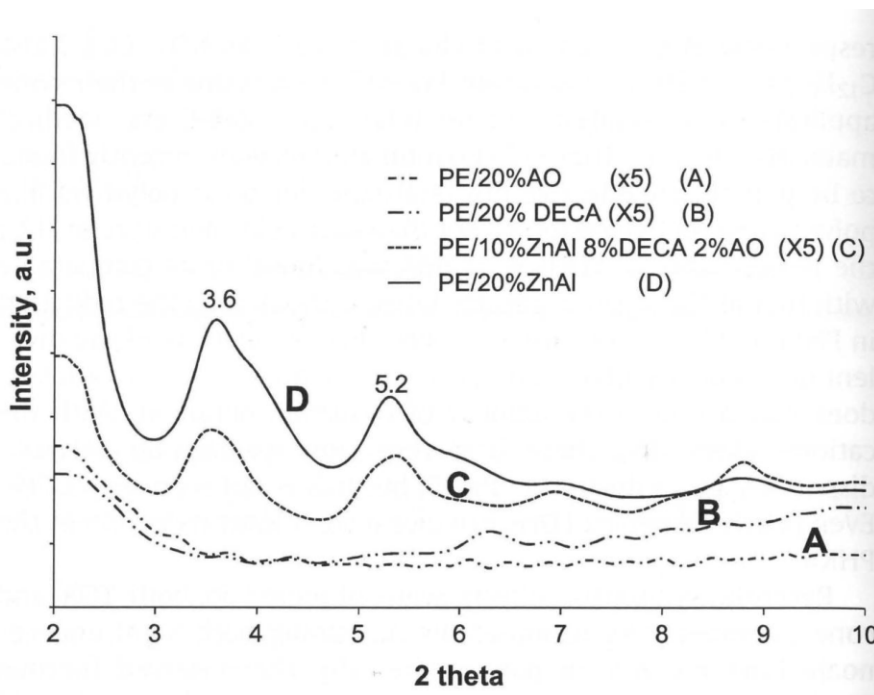
FT-IR of ZnAl oleate LDH (KBr pellet). (a) -OH group; (b) C-H stretching vibration for  $sp^2$  carbon of oleate anion; (c) C-H stretching vibration for  $sp^3$  carbon of undecenoate anion; (d)  $CO_2$  contaminant originating from baseline correction; (e) asymmetric stretch of  $RCOO^-$ ; (e') symmetric stretch of  $RCOO^-$ ; (f) scissoring bending vibration of C-H inplane bonds.

**Figure 2**



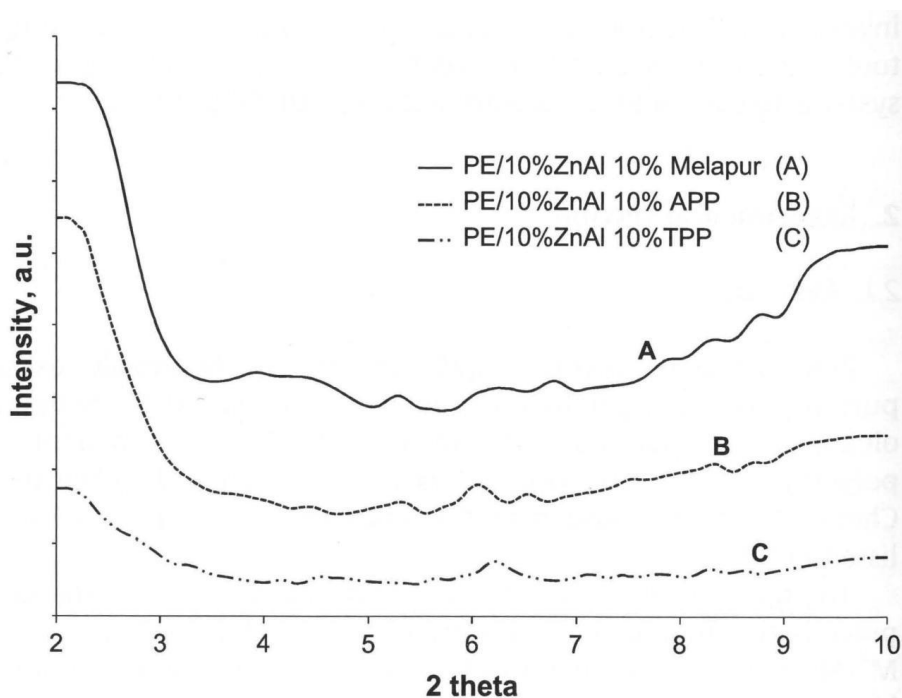
XRD trace of zinc aluminum oleate LDH (ZnAl).

**Figure 3**



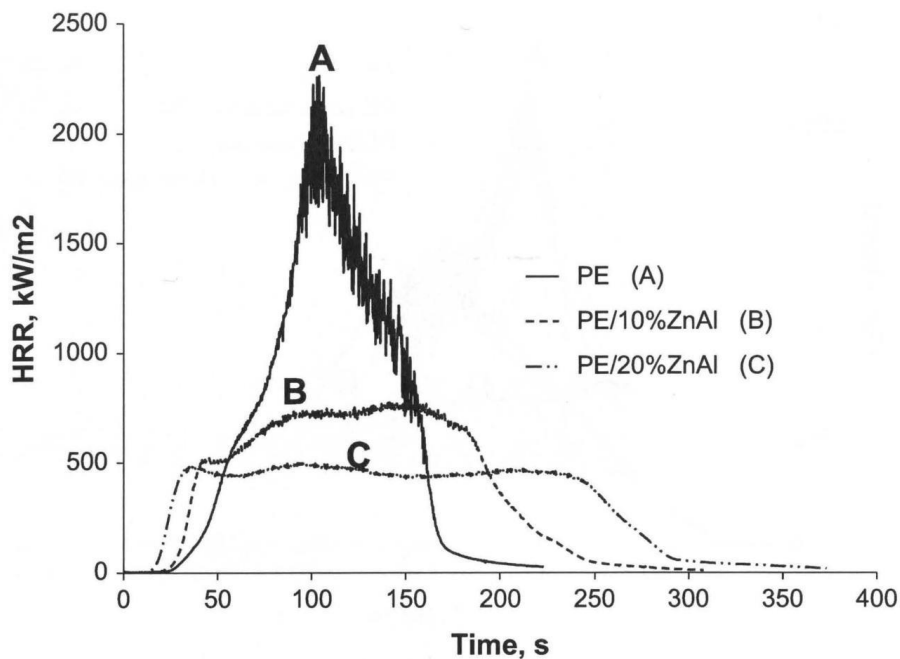
XRD traces of different combinations of DECA, AO, ZnAl with PE.

**Figure 4**



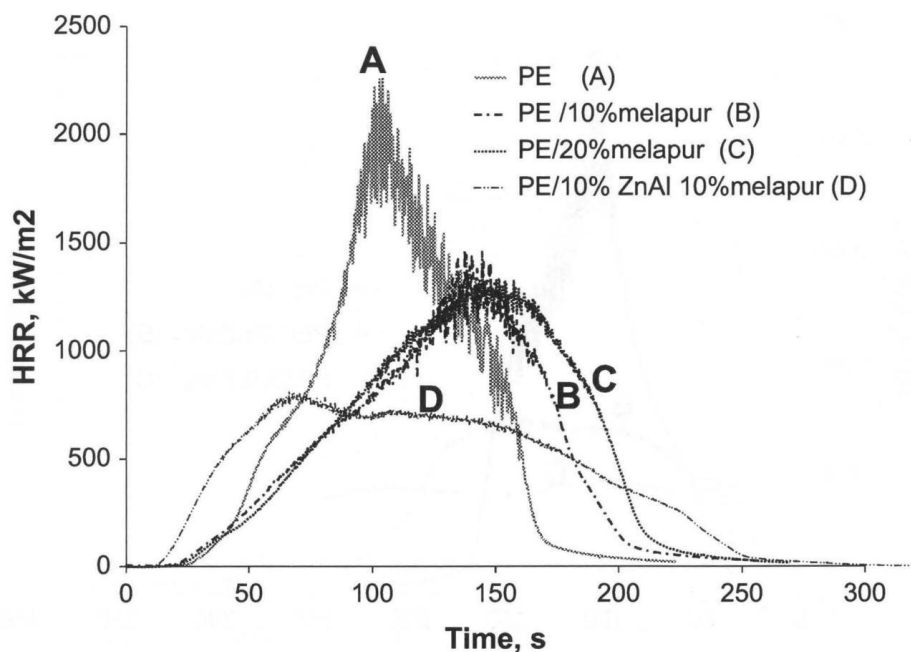
XRD traces of different combinations of MPP, APP, or TPP with PE.

**Figure 5**



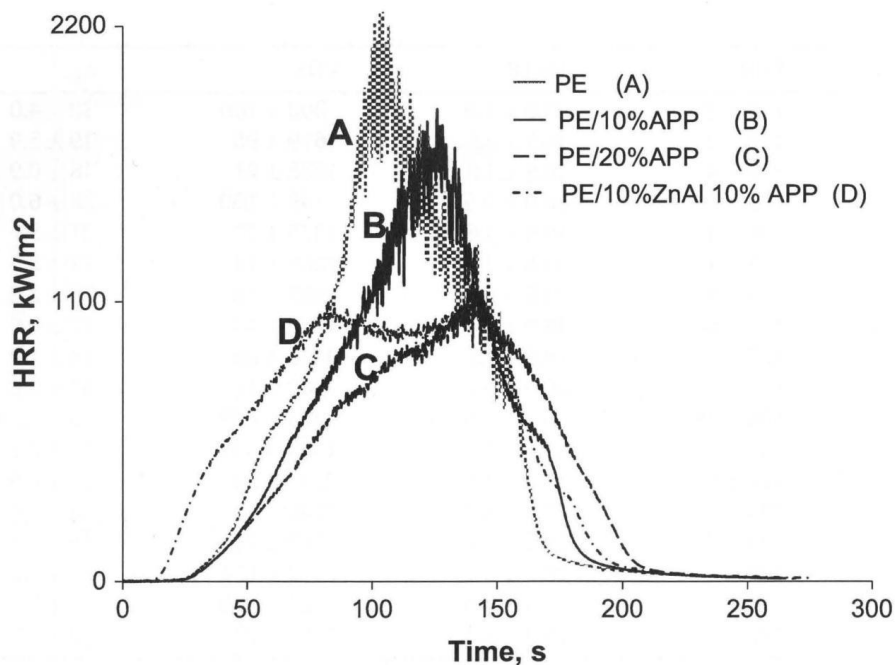
HRR curves of PE modified with 10% and 20% loadings of ZnAl (wt.%) at 50 kW/m<sup>2</sup>.

**Figure 6**



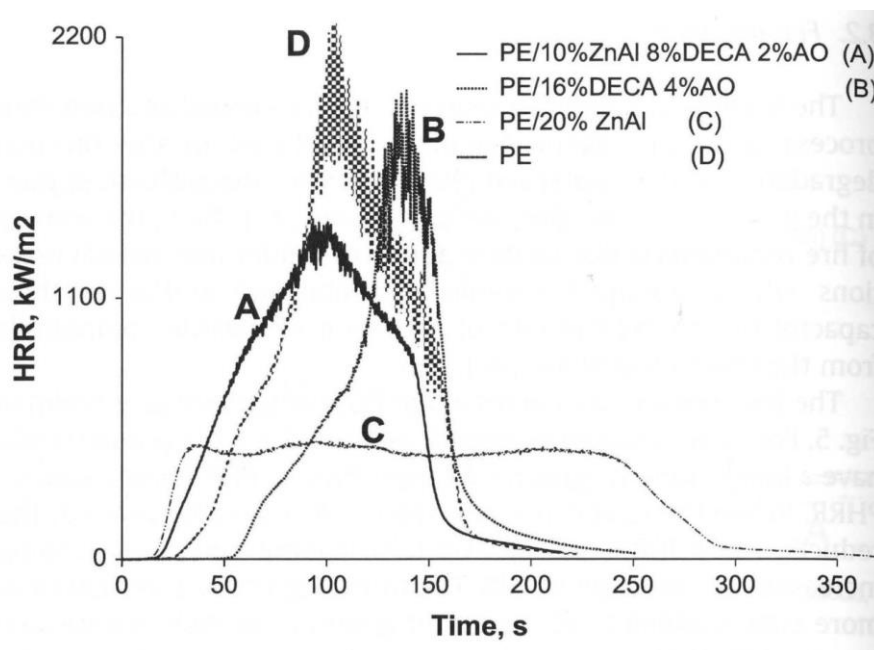
HRR curves of PE modified with MPP and LDH at 50 kW/m<sup>2</sup>.

**Figure 7**



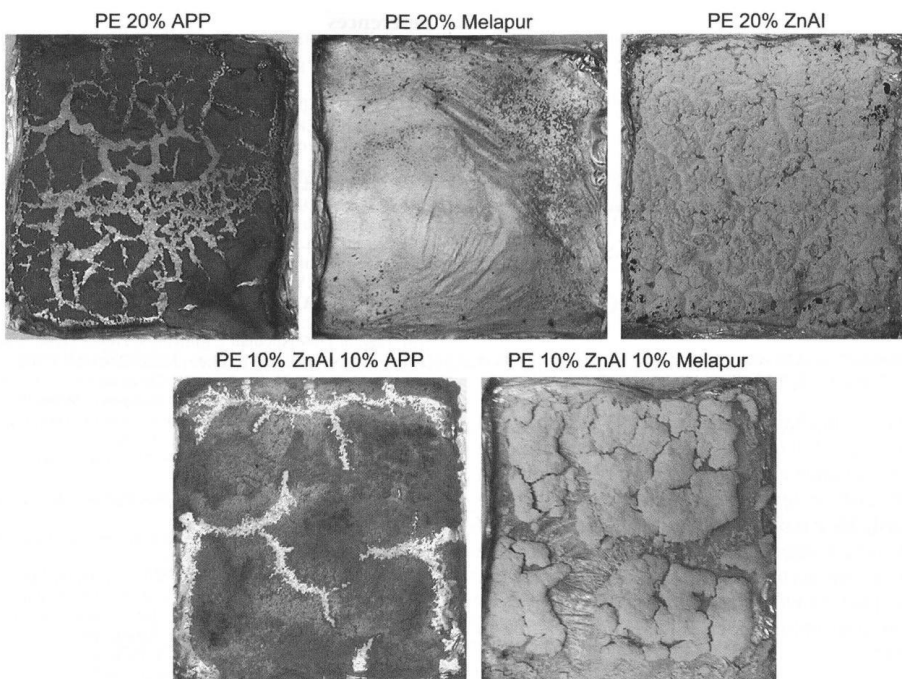
HRR curves of PE modified with APP and LDH at 50 kW/m<sup>2</sup>.

**Figure 8**



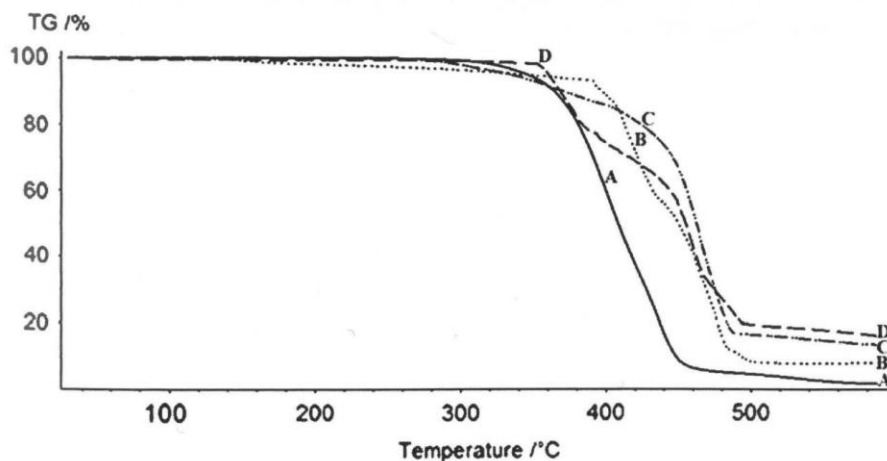
HRR curves of PE modified with DECA, AO and LDH at 50 kW/m<sup>2</sup>.

**Figure 9**



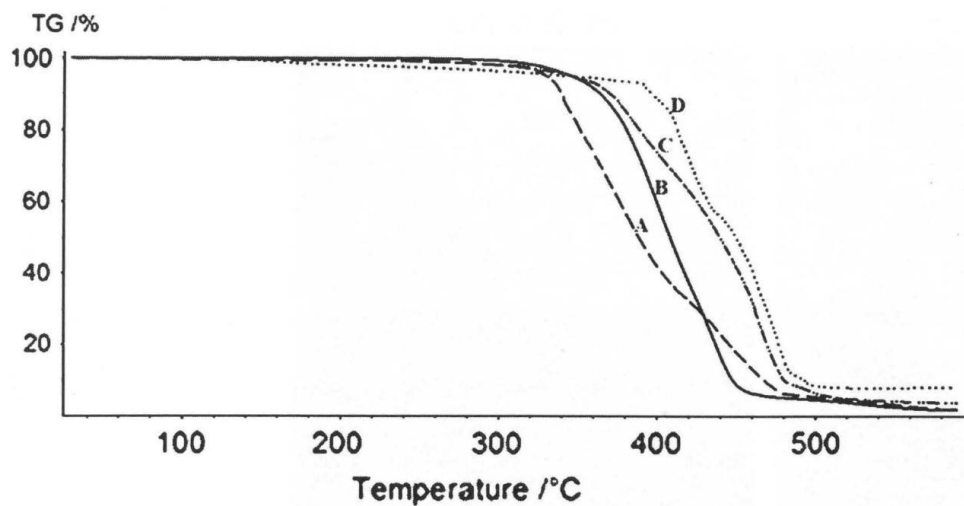
Pictures of the residues of selected modified PE systems after the cone experiment.  
Note: PE modified with RDP alone (or DECA, TPP) leaves no char after cone test.

**Figure 10**



TGA curves of the combinations of PE with ZnAl and APP in air environment at 20 °C/min. (A) PE; (B) PE/20%ZnAl; (C) PE/10%ZnAl 10%APP; (D) PE/20%APP.

**Figure 11**



TGA curves of the combinations of PE with ZnAl and MPP in air environment at 20 °C/min. (A) PE/20%MPP; (B) PE; (C) PE/10%ZnAl 10%MPP; (D) PE/20%ZnAl.