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2008 Sci. Technol. Adv. Mater. 9 024408

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Effect of clays on the fire-retardant properties of a polyethylenic copolymer containing intumescent formulation

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Received 21 December 2007

Accepted for publication 26 May 2008

Published 1 August 2008

Online at stacks.iop.org/STAM/9/024408

Abstract

Organophilic clay particles were added to a standard intumescent formulation and, since the role of clay expansion or intercalation is still a matter of much controversy, several clays with varying degrees of interlayer distances were evaluated. The composites were obtained by blending the nanostructured clay and the intumescent system with a polyethylenic copolymer. The flame-retardant properties of the materials were evaluated by the limiting oxygen index (LOI), the UL-94 rating and thermogravimetric analysis (TGA). The results showed that the addition of highly expanded clays to the ammonium polyphosphate and pentaerythritol formulation does not significantly increase the flame retardancy of the mixture, when measured by the LOI and UL-94. However, when clays with smaller basal distances were added to the intumescent formulation, a synergistic effect was observed. In contrast, the simple addition of clays to the copolymer, without the intumescent formulation, did not increase the fire retardance of the materials.

Keywords: flame retardancy, organophilic clays, intumescent formulation

1. Introduction

Nanocomposites and materials containing nanostructured particles have recently started to be used for improving the flame retardancy of polymers. The presence of nanoparticulate materials, such as exfoliated clays, within a polymeric matrix is known to reduce the peak heat release rate according to cone calorimetry analysis. However, although nanocomposites appear to be a possible alternative to conventional flame retardants, further improvements are still necessary to achieve lower levels of total heat release. Several authors have suggested that nanoparticles alone will probably not be able to achieve flame retardancy but can be used as one of the components in conventional flame-retardant systems to achieve adequate performance [1, 2]. Some other authors have attempted to obtain a synergy effect between flame-retardant intumescent systems and nanostructured particulate materials,

such as zeolites and spent-oil-cracking catalyst from FCC process [3–6].

In this study the fire retardant used was a standard intumescent formulation containing ammonium polyphosphate (APP) and pentaerythritol (PER). This system is free of halogens, and is therefore more environmentally friendly. Its flame-retarding mechanism is based on the formation of a swollen tumid carbonaceous surface layer called a ‘char’ [7]. This system provides thermal insulation and a protecting layer between the flame and the underlying polymer [8, 9]. The synergy agents chosen in this study were a series of nanostructured particles of montmorillonitic clays, since several studies have reported their use for obtaining flame-retardant properties in polymer materials without an intumescent formulation [10–13]. Moreover, it has already been shown by our research group that the addition of natural Brazilian montmorillonitic clays to a polymeric matrix

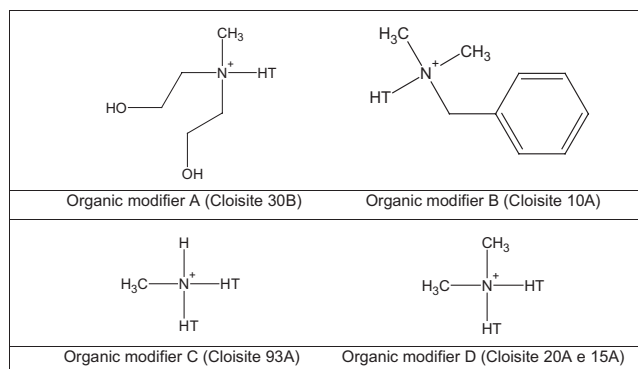


Figure 1. Compounds used in clay organophilization procedures. The symbol HT represents the hydrogenated tallow (approximately 65% C18, 30% C16 and 5% C14).

containing an intumescent formulation increases the amount of high-temperature residue. This synergistic effect was observed by TGA (Thermogravimetric Analysis) [14].

Therefore, the effect of the *d*-spacing of montmorillonites on the flame retardancy is of interest. Clays with different *d*-spacings have been shown to improve the fire-retardant properties of polymeric matrices such as EVA and PMMA, without the inclusion of intumescent systems [15, 16].

In the present study, several techniques were used to assess the flame retardancy potential of the produced materials and to evaluate the effect of the montmorillonite *d*-spacing, and also that of the nature and concentration of the organophilization agent used. The techniques used were thermogravimetric analysis (TGA), the limiting oxygen index (LOI), the UL-94 rating and heating microscopy.

2. Experimental

The polymer matrix used was a poly[ethylene (30%)–butyl acrylate] copolymer supplied by Elf–Atochem under the trade name Lotryl 3600, hereafter referred to as EBA-30.

The intumescent formulation studied was a mixture of APP, supplied by Hoechst under the trade name Exolit 422, and PER from Sigma Aldrich. APP acts both as an acid source and a foaming agent due to the evolution of ammonia on heating, and PER functions as a carbon source [17]. The APP:PER ratio was kept constant at 3, which is the ratio that, according to the literature, results in the maximum fire-retarding properties for polyethylenic materials [17].

The samples of montmorillonite were supplied by Southern Clay under the trade names of Cloisite Na⁺, Cloisite 30B, Cloisite 10A, Cloisite 93A, Cloisite 20A and Cloisite 15A. Cloisite Na⁺ is a natural clay but the other clays are organophilic with different *d*-spacings. Figure 1 shows the chemical structure of the organic modifiers used in the clay organophilization procedures. The information was given by the supplier.

The polymer and additives were mixed in a Haake Rheocord 9000 rheometer, equipped with a Rheomix 600 chamber and a Roller Blades rotor, at 160 °C while rotated at 50 rpm for 15 min. The clays were added to the polymeric mixture and accounted for 3 wt.% of the total mass involved.

Table 1. Chemical composition of Cloisite Na⁺.

Component	wt. (%)
Silicon oxide	61.78
Aluminum oxide	33.17
Iron (III) oxide	3.93
Potassium oxide	0.11
Calcium oxide	0.53
Titanium (IV) oxide	0.13
Sulfur	0.10
Chlorine	0.18
Scandium (III) oxide	0.02
Zirconium (IV) oxide	0.01
Zinc oxide	0.01
Strontium oxide	0.01
Others	0.01

The mixture was then pressed at 140 °C in a Carver press applying a 9000 kgf load on a 10 × 10 cm² area to obtain 3-mm-thick sheets, from which all the test specimens were produced.

The clays were characterized by different methods. The chemical composition was determined by x-ray fluorescence analysis using a Shimadzu EDX-700 x-ray spectrophotometer and the particle size distribution was determined in a Malvern Mastersizer Micro Plus (MAF 5001) analyzer. Textural analysis was carried out using a Micromeritics accelerated surface area and porosimetry analyzer (ASAP 2010), through which the specific surface area (S_{BET}) was obtained.

The carbon content of the samples was determined by CHN and TGA. These analyses were performed to identify the presence of organic compounds used in the organophilization of the montmorillonitic clays. The CHN analyses were carried out in a Thermo Finnigan, Flash EA1112 elemental analyzer. The TGA was performed using a Perkin-Elmer analysis system (Series 7).

The fire retardancy and thermal resistance of the materials obtained were evaluated by TGA, where the temperature shifts and the residual mass above 850 °C were regarded as an indication of the relative thermal stability. The samples were pulverized in a cryogenic mill, and during TGA 10 mg samples were heated at 10 °C min⁻¹ under a synthetic air flow of 20 cm³ min⁻¹.

The LOI tests were carried out in an FTT instrument using samples measuring 100 × 6.7 × 3 mm³, following the procedure described in the ISO 4589-2 standard. The materials produced were also rated according to the UL-94 (ANSI/ASTM D 635-77) standard.

The materials obtained were also submitted to heating microscopy. This method has proved to be a useful experimental technique for performing intumescence studies, since the phenomenon can be observed and monitored continuously *in situ* [18]. The analyses were carried out in a Leitz heating microscope (Model 1A) using cubic samples with a side of 3 mm, which were heated from 30 to 700 °C at a rate of 40 °C min⁻¹.

3. Results and discussion

The chemical composition of the natural clay (Cloisite Na⁺) is shown in table 1. The elemental analysis results for the

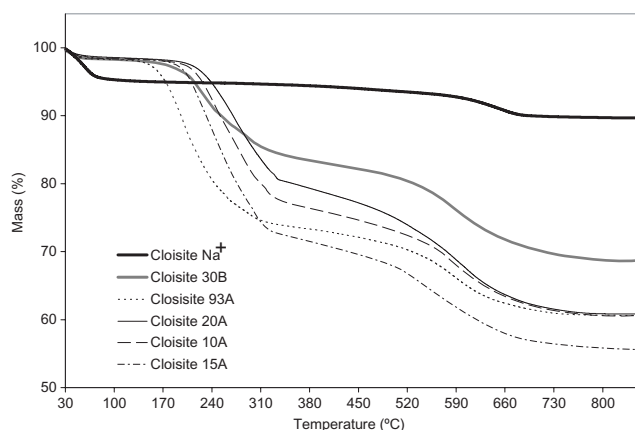


Figure 2. TGA curves of Cloisite Na⁺ and organophilic Cloisites.

clay are expressed in terms of the wt. % of its oxides. The high SiO₂ and Al₂O₃ contents in the montmorillonite clay are due to its crystalline structure. The silicon element is in the form of tetrahedral sheets, while the aluminum element is in the octahedral form [19, 20]. Silicon and aluminum oxides account for 94% of the total chemical composition of the clay.

The average particle size found in Cloisite Na⁺ was 10.7 μm and the specific surface area (S_{BET}) was 23.4 m² g⁻¹.

The organophilically modified Cloisites were analyzed by TGA and CHN. Figure 2 shows the TGA curves for all the Cloisites used in this work.

In figure 2 the weight loss at approximately 100 °C for Cloisite Na⁺ is due to the loss of hydration water. In the TGA curves for the organophilic Cloisites this loss is absent. The organophilization caused the replacement of the water molecules adsorbed on the clay surface by the organophilic agent, decreasing the amount of water on the surface of the clay. In the temperature range from 150 to 300 °C the organophilic Cloisites lost mass due to the thermal degradation of the organophilic agents. A further loss of weight, more pronounced than that for the natural clay, occurs in the range from 350 to 700 °C for Cloisite Na⁺. This loss represents only the dehydroxylation of the clay, but in organophilic clays the degradation of the organic compounds also occurs [19, 21].

Carbon analyses were carried out to quantify the amount of organophilization agent incorporated into the natural clay, and the results obtained are presented in table 2. Since natural clays contain small amounts of organic matter in their inorganic structure, the results for the organophilic clays were compared with that for the natural clay. However, this technique does not differentiate between carbon specimens located on the surface of the inorganic material and those that have effectively penetrated into the interlayer spacings.

Figure 3 shows the TGA curves for the polymeric materials with natural and organophilic clays. They show that the addition of Cloisite produced an increase of 40 °C in the thermal resistance of the matrix, but the residue at 850 °C was approximately 3% of the original sample, which corresponds to the amount of inorganic material added to the system. Thus, despite the fact that the clay causes an increase

Table 2. Carbon content in the natural and organophilic clays.

Nanoclay	Carbon content (% p/p)
Cloisite Na ⁺	0.0
Cloisite 30B	18.8
Cloisite 10A	27.8
Cloisite 93A	27.7
Cloisite 20A	28.2
Cloisite 15A	32.6

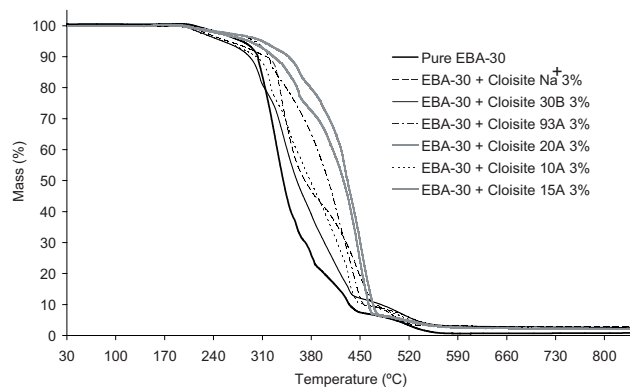


Figure 3. TGA curves of mixtures of EBA-30 with natural and organophilic Cloisites.

in the thermal resistance of the material, degradation occurs when high temperatures are reached. The increase in thermal stability may be caused by the formation of a carbonaceous structure rich in silica–aluminates, which would function as a thermal insulator [22].

Cloisites 10A, 20A and 15A, whose interlayer spacings are higher, produced an increase of up to 60 °C in the thermal resistance. However, in all cases, the material degraded completely at approximately 450 °C. Thus, regardless of the interlayer spacing, the addition of the clays did not prevent the complete degradation of materials at relatively low temperatures.

TGA was also performed to assess the effect of the addition of Cloisite clays in systems containing the intumescent formulation. Figure 4 shows that the addition of Cloisites did not increase the thermal resistance of the mixture of EBA-30 with the intumescent formulation, but it increased the amount of residue at 850 °C. The ratio between the high- temperature residue and mineral filler concentration in the system was 3.60 ± 0.18, which indicates an increase of more than three times the amount of clay added. All samples exhibited similar weight loss behavior. TGA was performed three times to obtain the above standard deviation.

Table 3 shows that the addition of Cloisite Na⁺ brought about an increase of 8 units for the LOI value in the mixture containing the intumescent formulation, while its addition to the pure polymer did not modify the LOI value.

The addition of the organophilic Cloisites does not modify the LOI value for the pure polymer. The differences observed are in the error range of the equipment. For systems containing the intumescent formulation, this measure shows that the addition of clays with higher interlayer spacings led to small improvements in the fire retardancy of the material.

Table 3. LOI values of the samples studied.

Clays added to the polymer mixture	Organic modifier ^a	Concentration of organic modifier (clay)	Basal distance (Å) ^b	LOI (vol.%)	
				Without APP/PER	With APP/PER
No clay added	—	—	—	19	21
Cloisite Na ⁺	—	—	11.7	19	29
Cloisite 30B	A	90 meq/100 g	18.5	19	29
Cloisite 10A	B	125 meq/100 g	19.2	19	28
Cloisite 93A	C	90 meq/100 g	23.6	18	29
Cloisite 20A	D	95 meq/100 g	24.2	19	24
Cloisite 15A	D	125 meq/100 g	31.5	20	23

^aThe schematic representation of each organic modifier is shown in figure 1.

^bInformation from the supplier.

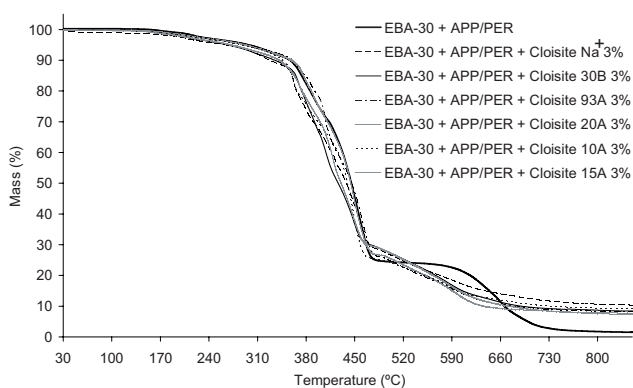


Figure 4. TGA curves of mixtures of EBA-30 with intumescent formulation added to natural and organophilic Cloisites.

A synergistic effect was observed between the clay and the intumescent system in the EBA-30 matrix for clays with *d*-spacings of up to approximately 24 Å. The material containing Cloisite Na⁺ and the intumescent formulation had an LOI value similar to those obtained for all the compounds containing organophilic clays with smaller spacings, even when a different type and concentration of organophilic agent was used. These results indicate that for small spacings, the organic modifier has little effect on fire retardancy. However, the addition of organophilic clays with interlayer spacings larger than 24 Å did not contribute significantly towards reducing the ease of ignition of mixtures of EBA-30 with APP/PER.

The effects of the type and concentration of the organophilic agents used on the flame retardancy were evaluated through the results obtained for some of the materials. Table 3 shows that the addition of Cloisite 10A (*d*-spacing = 19.2 Å; LOI = 28%) and Cloisite 15A (*d*-spacing = 31.5 Å; LOI = 23%) to materials containing the intumescent formulation leads to significantly different results. Considering that these clays have the same concentration of organic modifier (125 meq/100 g clay), the difference in flame retardancy observed could be due to either the nature of the organic compound used in the organophilization process or the *d*-spacing generated in the clay.

This effect can also be discussed through the results obtained for Cloisite 30B (*d*-spacing = 18.5 Å; LOI = 29%)

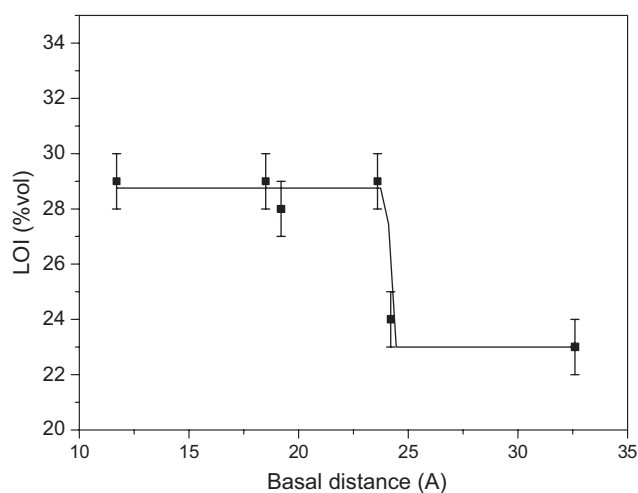


Figure 5. Effect of basal spacing of clay on the LOI values for samples with intumescent formulation.

and Cloisite 93A (*d*-spacing = 23.6 Å; LOI = 29%) since these clays have also the same concentration of different organic modifiers (90 meq/100 g clay). However, the addition of these clays led to the same excellent results. Cloisite 30B has an organic modifier that contains two hydroxyl groups that may enhance the formation of the intumescent layer. On the other hand, Cloisite 93A has an organic modifier containing an acid hydrogen that may also have a positive effect on fire retardancy. Although both these clays have organic modifiers with different chemical structures, the LOI values are the same as those obtained for the untreated Cloisite Na⁺. These results suggest that the type of organic modifier did not play a major role in the LOI results of the intumescent materials.

The effect of the concentration of the organic modifier can also be evaluated through some other results. Cloisite 20A (*d*-spacing = 24.2 Å; LOI = 24%) and 15A (*d*-spacing = 31.5 Å; LOI = 23%) were added to the matrix containing APP/PER. These clays have the same organophilization agent (D in figure 1), but in different concentrations (table 3). Despite the different concentrations, the samples had very similar LOI values. These results seem to indicate that the *d*-spacing of the clay is more significant in affecting the LOI value than the type and concentration of the organophilization agent used. The results in table 3 indicate that clays with *d*-spacings lower than 24 Å can produce materials with LOI

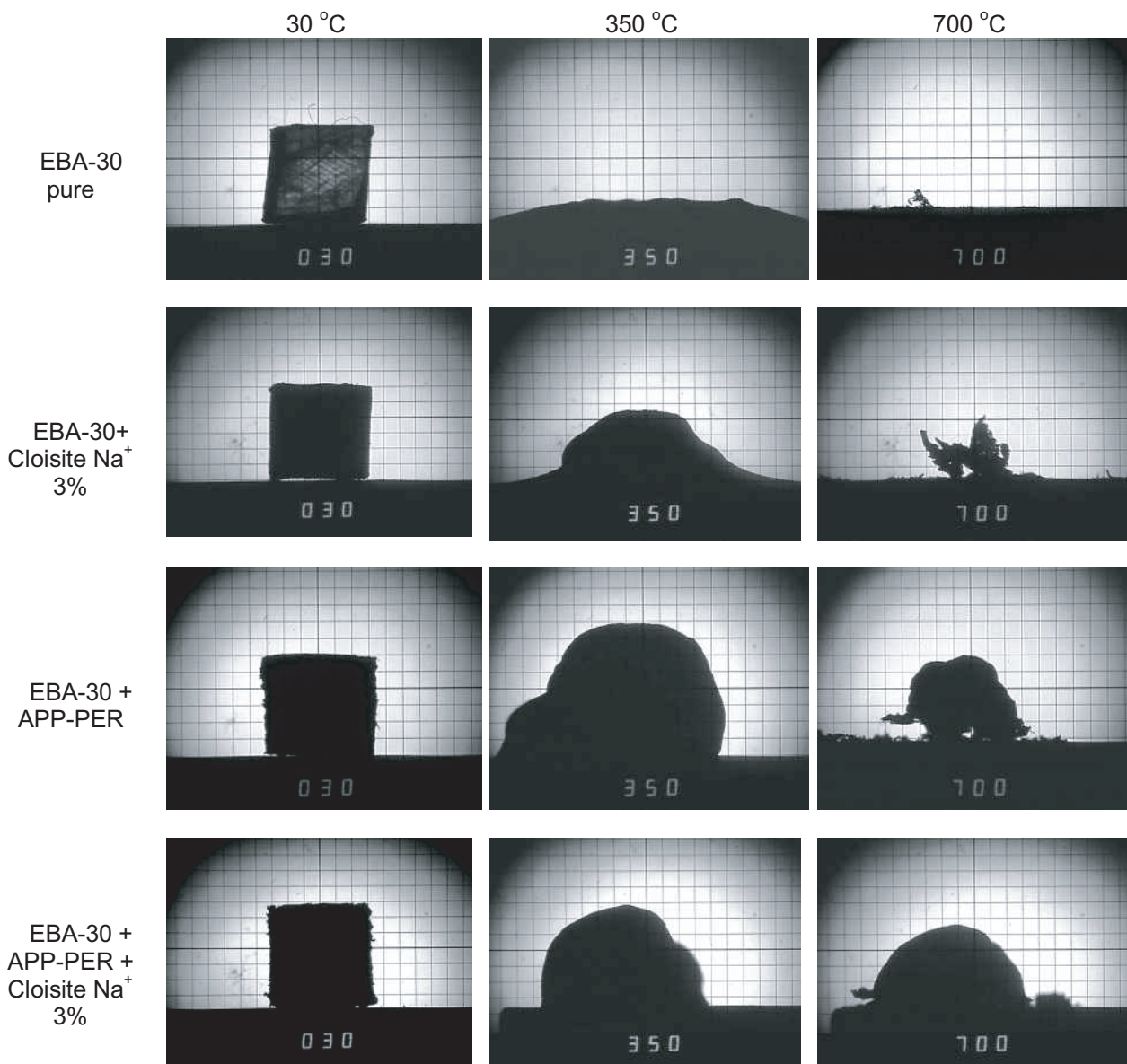


Figure 6. Heating microscopy images of EBA-30 systems at 30, 350 and 700 °C (± 1 °C).

values of approximately 29, regardless of the presence of organophilic agents. Moreover, clays with interlayer spacings close or greater than 24 Å do not exhibit a strong synergistic effect. Figure 5 shows the relationship between the basal spacing of the clay and the LOI value for the materials.

Compounds of EBA-30 with 3% silica and 3% alumina were obtained to assess the effect of the silicon and aluminum elements, which are present in large amounts in the clays. A third compound consisting of a physical mixture of both oxides was also prepared. The same compounds were also incorporated in the intumescent formulation. The values of LOI obtained are shown in table 4. The results show that the addition of silica and alumina separately does not change the LOI value of the pure polymer. The physical mixture of both oxides also did not change the LOI value of the matrix. For samples containing the intumescent formulation, the low efficiency of the compounds containing only silica or alumina

Table 4. LOI values of materials containing silica and alumina.

Sample	%LOI (± 1)	
	Without APP/PER	With APP/PER
EBA-30	19	21
EBA-30 + Silica 3%	19	22
EBA-30 + Alumina 3%	19	22
EBA-30 + Si/Al (2,34:1) 3%	19	22

is observed. Furthermore, the low LOI value for the material with the intumescent formulation and the physical mixture of silica and alumina shows that the presence of both elements is not sufficient to achieve the synergistic effect desired.

Estevão and coworkers [23, 24] observed that silica-aluminates, such as kaolin and zeolites, are better flame retardancy enhancers than silica and alumina alone in

Table 5. UL-94 ratings of the samples.

Sample	Rating
EBA-30	Not rated
EBA-30 + Cloisite Na ⁺ 3%	Not rated
EBA-30 + Cloisite 30B 3%	Not rated
EBA-30 + Cloisite 15A 3%	Not rated
EBA-30 + APP/PER	V0
EBA-30 + APP/PER Cloisite Na ⁺ 3%	V0
EBA-30 + APP/PER + Cloisite 30B 3%	V0
EBA-30 + APP/PER + Cloisite 15A 3%	V2

mixtures containing an intumescent formulation. Thus, it is proposed that the elements Si and Al should be present in a specific structure, such as in the form of kaolin, zeolites or montmorillonites.

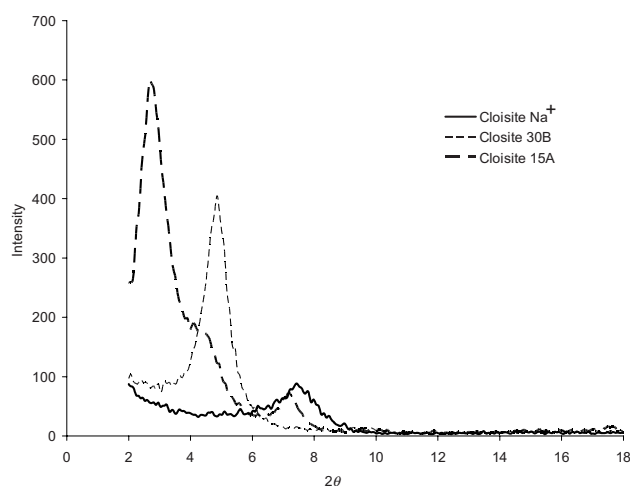
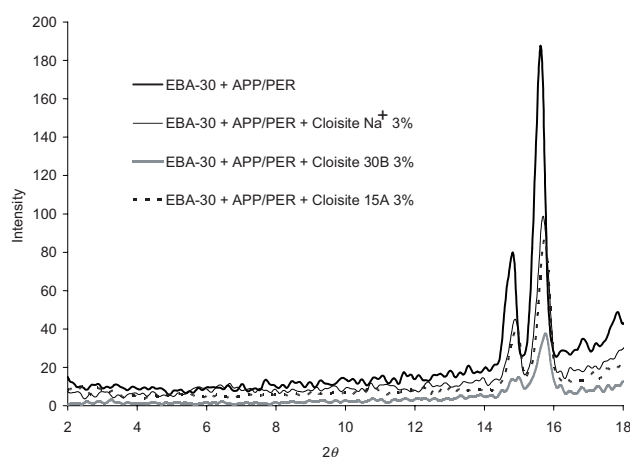
The above results indicate that when the interlayer spacing exceeds 24 Å, the structure of the clay necessary for synergy to occur begins to disappear, markedly reducing the synergistic effect. Thus, the Cloisite Na⁺ had a similar LOI value to the organophilic clays with *d*-spacings close to 23 Å. For this interlayer spacing the necessary structure was maintained.

Therefore, it seems that the concentration and chemical structure of the organic modifier have little influence on the extent of the synergistic effect shown in table 3. The material with Cloisite Na⁺ had an LOI value equivalent to those obtained with the organophilic clays with *d*-spacings of approximately 23 Å (Cloisite 30B, Cloisite 10A and Cloisite 93A). All these clays have different types and concentrations of organophilic agents. Cloisite 10A, for example, contains the highest concentration of the modifier. However, the intumescent sample containing this clay had the highest LOI value (table 3), showing that the large number of inflammable small organic molecules of the organophilic agent did not have a detrimental effect upon the fire-retardant properties of the system.

On the basis of the LOI results, UL-94 tests were performed on compounds containing the Cloisites Na⁺, 30B and 15A. Table 5 shows the UL-94 ratings of the samples. The results show that the addition of Cloisites did not change the UL-94 rating of the pure polymer. The addition of Cloisite Na⁺ and 30B clays to the mixtures containing the intumescent formulation resulted in the maximum classification V0. However, the material with Cloisite 15A, which has a *d*-spacing larger than 30 Å, had a V2 rating, since the system dripped during burning. Thus, an excessive increase in the *d*-spacing also affects the rheological properties and consequently, the efficiency of flame retardancy. These results are in agreement with the LOI values, which exhibited a decrease in synergy when excessively expanded clays were used.

Heating microscopy was used for the systems produced to monitor the intumescence process during the burning of the materials. Figure 6 shows images obtained at 30, 350 and 700 °C.

The images show that the polymeric matrix degraded completely at 350 °C, since the clay, as the only additive, did not provide any additional protection to the system. The

**Figure 7.** XRD patterns of Cloisites before processing.**Figure 8.** XRD patterns of polymeric mixtures containing intumescent formulation and Cloisites after processing.

addition of the intumescent formulation led to the formation of a char, giving more protection to the polymer. The images show the swelling of the structured layer of this system. The presence of clay in the intumescent system helped to maintain the carbonaceous structure at 700 °C. When this temperature was reached, the structure generated in the system containing only APP/PER had already collapsed.

The morphology of the clays within the EBA-30 matrix containing APP/PER was evaluated by x-ray diffraction (XRD). The materials containing the intumescent formulation and Cloisites Na⁺, 30B and 15A were chosen because they had the lowest and highest basal spacings out of those studied. Figure 7 shows the XRD patterns of the Cloisites before processing and figure 8 shows the XRD patterns of the polymeric mixtures containing the clays and the intumescent formulation after processing. It can be observed that the peak from each clay (as shown in figure 7) disappeared upon processing. However, it was not possible to prove the occurrence of delamination or intercalation of the clays during processing, and therefore the formation of a genuine nanocomposite.

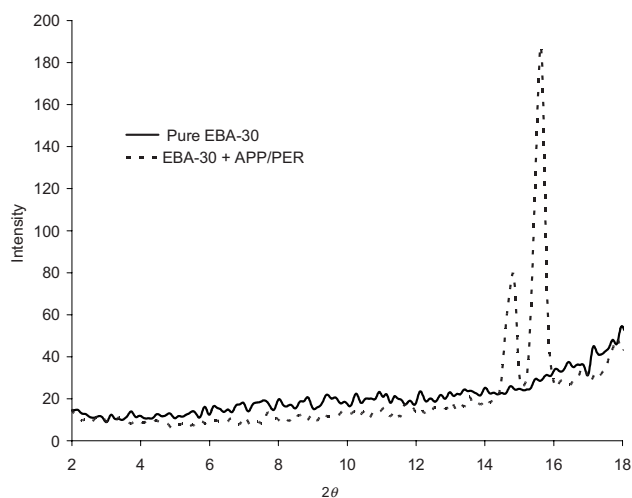


Figure 9. XRD patterns of pure polymer with and without clay.

Figure 9 shows XRD results for the EBA-30 and EBA-30+APP/PER samples. The polymer did not have a crystalline structure. Thus, the XRD peaks for the sample containing the intumescent formulation are associated only with the APP/PER additives.

4. Conclusions

Clays with several interlayer distances and different types and concentrations of organophilic agent were incorporated into a polyethylenic copolymer containing an intumescent formulation.

All the techniques employed to evaluate the materials showed that the addition of the untreated Cloisite Na⁺ to the intumescent material brought about a significant improvement in the flame retardancy of the composites. A synergistic effect was observed between the intumescent components of the material and the natural clay. However, this effect was not observed when the natural clay was added to the polymeric matrix without the presence of the intumescent components.

The effect of the basal spacing of the clay and of the type and concentration of the organic modifier on the fire-retardant properties of materials containing an intumescent formulation were evaluated through the use of differently treated clays. The results indicate that the *d*-spacing has a more prominent effect on determining the synergistic potential amongst the additives than the type and concentration of the organophilic agent used. Clays with *d*-spacings of up to 24 Å produced the same synergy effect as that obtained for the untreated clay (11.7 Å). The results suggest that when the interlayer spacing exceeds 24 Å, the structure of the clay necessary for synergy

to occur begins to disappear, markedly reducing the synergistic effect.

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