

SYNTHESIS, FLAME-RETARDANT AND SMOKE-SUPPRESSANT PROPERTIES OF A BORATE-INTERCALATED LAYERED DOUBLE HYDROXIDE

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Abstract—Reaction of a Mg–Al carbonate layered double hydroxide (LDH) with boric acid leads to a borate-pillared LDH with the stoichiometry $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{B}_3\text{O}_5]_{0.35}\cdot 0.65\text{H}_2\text{O}$ and an interlayer spacing of 1.07 nm. Infrared and ^{11}B magic angle spinning nuclear magnetic resonance data are consistent with the presence of polymeric triborate anions of the type $[\text{B}_3\text{O}_4(\text{OH})_2]_n^{n-}$ in the interlayer galleries so that the material can be formulated as $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{B}_3\text{O}_4(\text{OH})_2]_{0.35}\cdot 0.30\text{H}_2\text{O}$. The flame-retardant properties of the borate-pillared material and the carbonate precursor in composites with ethylene vinyl acetate copolymer were compared. Introduction of the borate anion leads to a significant enhancement in smoke suppression during combustion without compromising the flammability of the material. This is related to the synergistic effect between the host layers of the LDH and the borate anions uniformly distributed in the interlayer region.

Key Words—Borate, Flame Retardant, Hydrotalcite, Layered Double Hydroxide, LDH, Smoke Suppressant.

INTRODUCTION

The global annual market for flame retardants (FRs) is estimated to be \$2.4 billion with growth of ~5% per annum (Tullo, 2000). In recent years there has been increasing concern about the environmental hazards associated with halogen-containing FRs because of the toxicity of the products formed during a fire or when incinerating or recycling waste plastics. As a consequence, there has been considerable interest in halogen-free flame retardants and metal hydroxides such as aluminum hydroxide (ATH) (Hippi *et al.*, 2003) and magnesium hydroxide (MH) (Mai *et al.*, 2003) are already in commercial use. Recent studies (Camino *et al.*, 2001) have shown that a layered double hydroxide (LDH) (Cavani *et al.*, 1991; Khan and O'Hare, 2002) with the formula $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3\cdot 3\text{H}_2\text{O}$ has better flame-retardant properties than either ATH or MH and that the layered structure may play a key role in this respect. The LDHs can be represented by the general formula $[\text{M}_1^{\text{II}}\text{xM}_2^{\text{III}}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}$. The mineral hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$) is an example of one such material and LDHs are also known as hydrotalcite-like materials.

In addition to improving resistance to ignition, a second key property of FRs is the ability to suppress smoke production if a fire does occur, because the majority of deaths in such instances are a result of suffocation. Although metal hydroxides do have limited

smoke-suppressing properties (Kim, 2003), other additives such as zinc borates (*e.g.* Firebrake[®] 415 ($4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$)) are often combined with MH (Carpentier *et al.*, 2000a, 2000b; Durin-France *et al.*, 2000) or ATH (Ning and Guo, 2000). The borate promotes the formation of a ceramic-like MgO - or Al_2O_3 -based coating that forms over the char which forms on the surface of a polymer during combustion and subsequently forms a vitreous phase which acts as a binder to reinforce this ceramic coating preventing further combustion (Carpentier *et al.*, 2001).

Here we report the synthesis and flame-retardant properties of an LDH containing borate ions intercalated in the interlayer region. This material should have two advantages over existing FRs based on physical mixtures of zinc borate and ATH or MH: (1) LDHs themselves have superior flame-retardant properties to ATH or MH (Camino *et al.*, 2001); and (2) intercalation of the borate anion in the interlayer region of the LDHs will give a uniform dispersion of the two active phases at the molecular level which should give rise to enhanced synergistic effects (Durin-France *et al.*, 2000).

EXPERIMENTAL

Reagents

The reagents were all of analytical grade, obtained locally and used without further purification.

Synthesis of the LDH carbonate precursor

The LDH carbonate precursor was prepared using a method developed recently in our laboratory (Zhao *et al.*, 2002). The ratios of the components in the synthesis mixture were as follows: $[\text{Mg}^{2+}]:[\text{Al}^{3+}] = 2.0$; $[\text{NaOH}]$:

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$[\text{Mg}^{2+} + \text{Al}^{3+}] = 1.6$; $[\text{CO}_3^{2-}] : [\text{Al}^{3+}] = 2.0$. A portion of the product was dried at 100°C for 24 h for analysis, but the remainder was stored as a moist filter cake and not allowed to dry out.

Synthesis of borate-pillared LDH

A solution of 3.2 M H_3BO_3 in distilled water was added dropwise to a stirred suspension of the LDH carbonate filter cake (which was 22% solid by weight, or 0.45 mmol) in water (10 mL) until the pH of the mixture was 3.5. The stirred mixture was heated at 100°C for 2 h. The resulting precipitate was filtered, washed well with water and dried at 70°C for 24 h. Elemental analysis of the precipitate (wt.%), which was consistent with the formula $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2] [\text{B}_3\text{O}_5]_{0.35} \cdot 0.65\text{H}_2\text{O}$, gave Mg 14.3 (14.3 calculated); Al 9.4 (8.6); B 9.5 (10.3); C 0.38 (0.00); and H_2O 10.0 (10.6).

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, $\text{CuK}\alpha$ ($\lambda = 0.15406$ nm) radiation. The samples, as unoriented powders, were scanned in steps of $0.02^\circ 2\theta$ in the range $3-70^\circ 2\theta$ using a count time of 4 s per step. Elemental analyses (Mg, Al, B) were performed by ICP emission spectroscopy using an Ultima instrument on solutions prepared by dissolving the samples in dilute HNO_3 . Fourier transform infrared (FTIR) spectra were obtained on a Bruker Vector 22 spectrometer using the KBr pellet technique. Water content and thermal decomposition were monitored by thermogravimetric (TG) and differential thermal analysis (DTA), using a PCT-1A thermal analysis system produced locally, with a heating rate of $10^\circ\text{C}/\text{min}$ in air. Samples were pre-dried in air at 70°C for 24 h. The ^{11}B MAS NMR spectra were recorded on a Bruker AV-300 spectrometer, operating at 96.3 MHz for boron in a 5 mm probe with a spinning frequency of 13 kHz, pulse duration of 2 μs and delay parameter of 3 s. Chemical shifts are referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

Polymer compounding

EVA-28 (containing 28% vinyl acetate) and the LDH (60 wt.%) were mixed for 15 min in a twin roller mixer, operating at a temperature of 140°C. The resulting materials were molded into flat sheets with thickness of 1 or 3 mm using a compression molder at a temperature of 150°C and an applied pressure of 3.9 MPa.

Combustion tests

Limiting oxygen index (LOI) values were determined with an FTA II instrument (PL Co., United Kingdom). Measurements were taken on a sample measuring $100 \times 6.5 \times 3$ mm according to the Chinese National Standard GB/T2406-93. Smoke-density measurements were taken with an SD-2A smoke density analyzer

(Luoyang Ship Material Research Institute), using the ASTM E 662-95 method, on a sample measuring $75 \times 75 \times 1$ mm.

RESULTS AND DISCUSSION

Synthesis and characterization of borate-pillared LDH

The most common methods of preparation of LDHs are (Cavani *et al.*, 1991; Khan and O'Hare, 2002): (1) coprecipitation; and (2) ion exchange of a preformed LDH containing Cl^- or NO_3^- ions. There have been several reports in the literature of borate-pillared LDHs prepared using these methods (Bhattacharya and Hall, 1992; Li *et al.*, 1996; Lin *et al.*, 1999; del Arco *et al.*, 2000; Bechara *et al.*, 2002). In the case of the coprecipitation reactions, the crystallinity of the products is relatively low and in the case of the exchange reactions it is necessary to work under a nitrogen atmosphere in order to avoid competitive intercalation by carbonate ions arising from atmospheric carbon dioxide.

In order to prepare a crystalline borate-pillared LDH in a simple process which can be readily scaled up, we start with a preformed highly crystalline LDH carbonate. Such materials are the easiest variant of LDHs to prepare, but the interlayer carbonate ion is tenaciously held between the layers and may not be easily displaced by other anions in ion-exchange reactions (Cavani *et al.*, 1991; Khan and O'Hare, 2002). It is known, however, that the carbonate ion may be converted to CO_2 by reaction with either aqueous acid solutions (Bish, 1980; Costantino *et al.*, 2000) or gaseous HCl (Costantino *et al.*, 1998), with concomitant intercalation of the conjugate base of the acid.

A Mg-Al carbonate containing LDH (Mg/Al = 2) was synthesized by a method developed recently in our laboratory (Zhao *et al.*, 2002). The powder XRD pattern of the dried LDH-carbonate precursor (Figure 1a) exhibits the characteristic (Cavani *et al.*, 1991; Khan and O'Hare, 2002) diffraction lines of LDH materials with a series of $00l$ peaks appearing as narrow symmetric lines at low angle corresponding to a basal spacing of 0.76 nm and higher-order reflections. No other crystalline phase was detected.

A sample of the undried Mg-Al carbonate LDH filter cake was suspended in water and a solution of boric acid added, resulting in effervescence due to liberation of CO_2 . The amount of boric acid was chosen so as to give a final pH of the reaction mixture of 3.5. The powder XRD pattern of the product (Figure 1b) also exhibits the characteristic reflections (Cavani *et al.*, 1991; Khan and O'Hare, 2002) of LDH materials. No other crystalline phases are obtained under these conditions; if the final pH is >4.0 , a mixture of phases, including incompletely exchanged carbonate-pillared LDHs are obtained. The XRD peaks are narrow, indicating that the high crystallinity of the precursor has been maintained. The basal

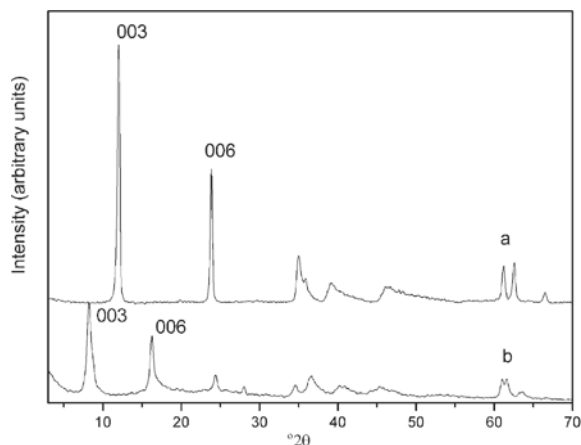


Figure 1. Powder XRD patterns of (a) Mg-Al LDH carbonate and (b) borate-pillared LDH. The basal reflection 003 shows a shift to lower angle after intercalation of the borate anion, indicating an increase in layer spacing.

spacing in the borate-pillared LDH is 1.07 nm, some 0.31 nm greater than the carbonate precursor. Since the thickness of the LDH sheet is 0.48 nm, the gallery height in the borate-pillared LDH is 0.59 nm. The solution chemistry of the aqueous borate system is complex and a large number of different anions can be obtained under different conditions of pH and concentration (Farmer, 1982). At intermediate pH values, the monovalent species $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ and $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ predominate with increasing amounts of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ and $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ being formed as the pH is increased (Farmer, 1982). Finally at high pH values, the mononuclear species $\text{B}(\text{OH})_4^-$ is formed. A gallery height of 0.59 nm is similar to that reported (Bhattacharya and Hall, 1992) for triborate anions of the type $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ intercalated perpendicular to the cationic layers.

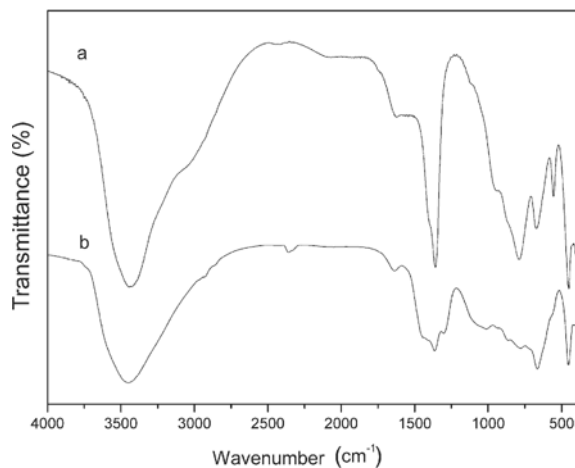


Figure 2. IR spectra of (a) Mg-Al LDH carbonate and (b) borate-pillared LDH. In (b), bands between 1500 and 1250 cm^{-1} can be assigned to $\nu_3 \text{BO}_3$ stretching modes and those between 1200 and 800 cm^{-1} to $\nu_3 \text{BO}_4$ -stretching modes.

Analytical data for the borate-pillared LDH are consistent with the formulation $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{B}_3\text{O}_5]_{0.35}\cdot 0.65\text{H}_2\text{O}$. The triborate anion $[\text{B}_3\text{O}_5\cdot y\text{H}_2\text{O}]^-$ may exist in different structural forms depending on the extent of hydration (Touboul *et al.*, 2003) and the structure of the anion present in the borate-pillared LDH can be explored further by infrared (IR) and NMR spectroscopy.

The IR spectrum for the borate-pillared LDH (Figure 2) shows strong, broad bands between 1500 and 1250 cm^{-1} which can be assigned to $\nu_3 \text{BO}_3$ -stretching modes and bands between 1200 and 800 cm^{-1} which can be assigned to $\nu_3 \text{BO}_4$ -stretching modes (Li *et al.*, 1996; del Arco *et al.*, 2000; Peak *et al.*, 2003). The $\nu_3 \text{BO}_3$ -stretching modes would obscure any band due to carbonate (its ν_3 -stretching mode occurs around 1360 cm^{-1}) not displaced by reaction with boric acid, but the very small carbon content (B/C ratio of 28:1) and the absence of any effervescence when the borate-pillared LDH was dissolved in dilute HCl confirms the absence of any significant amounts of carbonate. The spectrum shows significant differences from that of the isolated $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ anion found in $\text{KB}_3\text{O}_5\cdot 3\text{H}_2\text{O}$ (Salentine, 1987) and the mineral ameghinite ($\text{NaB}_3\text{O}_5\cdot 2\text{H}_2\text{O}$) (Dal Negro *et al.*, 1975), both of which have been structurally characterized. The spectrum is, however, very similar to that of the material obtained by gentle heating of $\text{KB}_3\text{O}_5\cdot 3\text{H}_2\text{O}$, which has the stoichiometry $\text{KB}_3\text{O}_5\cdot x\text{H}_2\text{O}$ ($x \approx 1$) and contains polymeric borate anions (Salentine, 1987). The related material $\text{TIB}_3\text{O}_5\cdot 1.5\text{H}_2\text{O}$ has been structurally characterized (Touboul *et al.*, 1983) and shown to contain chains of $[\text{B}_3\text{O}_4(\text{OH})_2]_n^-$ anions, with each B_3 entity composed of one tetrahedral BO_4 unit and two trigonal planar BO_3 units, *i.e.* structural type 3: $\infty(2\Delta + T)$ in the usual classification (Touboul *et al.*, 2003) of borate anions.

The TG-DTA curves for the borate-pillared LDH are shown in Figure 3. An initial weight loss of 10.0%

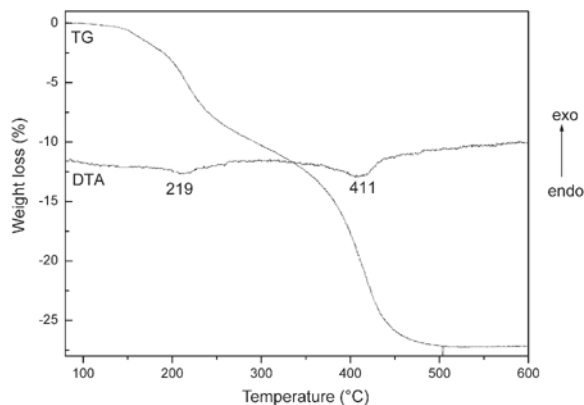


Figure 3. TG-DTA curves for the borate-pillared LDH. Weight loss below 300°C can be attributed to loss of surface and interlayer water whilst that between 300 and 600°C is associated with decomposition of the borate anion and dehydroxylation of the layers.

between room temperature and 300°C is observed with a corresponding endotherm in the DTA at 219°C. This weight loss can be attributed to loss of surface and interlayer water and dehydration of the borate anion as has been observed for isolated triborate anions intercalated in LDHs (Bhattacharya and Hall, 1992). The weight loss is consistent with the proposed stoichiometry of the material given above (calculated weight loss 10.6%). A further weight loss of 16.7% occurs between 300 and 600°C associated with the decomposition of the triborate anion and dehydroxylation of the layers, giving a total weight loss of 26.7%. Decomposition of the borate-pillared LDH according to the stoichiometry $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{B}_3\text{O}_5]_{0.35}\cdot 0.65\text{H}_2\text{O} \rightarrow 0.65\text{MgO} + 0.175\text{Al}_2\text{O}_3 + 0.525\text{B}_2\text{O}_3$ requires a weight loss of 27.0%.

The ^{11}B MAS NMR spectrum of the borate-pillared LDH is shown in Figure 4. The complex line shape can be interpreted in terms of the overlap of a fairly sharp singlet at 1.6 ppm associated with tetrahedrally coordinated boron and a second-order quadrupolar pattern characteristic of boron in trigonal sites. It is not straightforward to obtain the intensity ratio of the two types of boron sites by simple deconvolution of the spectrum (Li *et al.*, 1996; Tagg *et al.*, 1999) but the observation of signals from both BO_3 and BO_4 units is consistent with the presence of polymeric $[\text{B}_3\text{O}_4(\text{OH})_2]_n^{2-}$ anions as proposed above.

On the basis of the above data, we propose that borate-pillared LDH material contains polymeric $[\text{B}_3\text{O}_4(\text{OH})_2]_n^{2-}$ anions (i.e. $[\text{B}_3\text{O}_5\cdot y\text{H}_2\text{O}]^-$ with $y = 1$) and has the formula $[\text{Mg}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{B}_3\text{O}_4(\text{OH})_2]_{0.35}\cdot 0.30\text{H}_2\text{O}$. The borate anions have $-\text{B}-\text{O}-\text{B}-$ chains of BO_4 units oriented parallel to the layers with each BO_4 unit forming a hexagonal B_3O_3

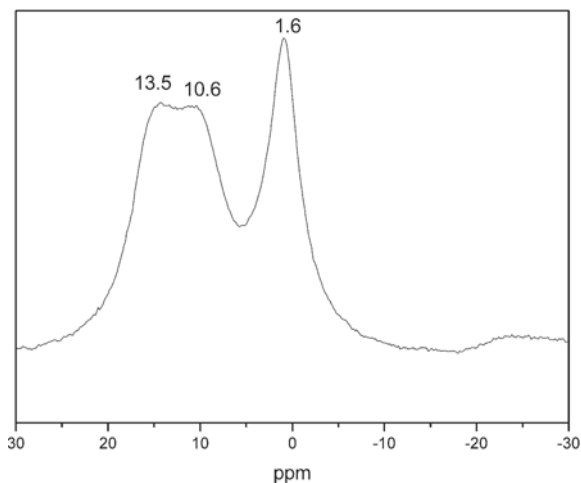


Figure 4. ^{11}B MAS NMR spectrum for the borate-pillared LDH. The sharp singlet at 1.6 ppm arises from tetrahedrally coordinated B and the remainder of the spectrum from a second-order quadrupolar pattern characteristic of B in trigonal sites.

ring with two BO_3 units; these rings are oriented perpendicular to the layers. Molecular models suggest that the expected interlayer spacing for this conformation is similar to that for isolated triborate anions of the type $[\text{B}_3\text{O}_3(\text{OH})_4]^-$ intercalated perpendicular to the cationic layers of LDHs (Bhattacharya and Hall, 1992) consistent with the XRD results discussed above.

Flame-retardant properties of the borate-pillared LDH

The flame-retardant properties of the LDH-carbonate precursor and the borate-pillared LDH were compared using an ethylene vinyl acetate copolymer containing 28 wt.% vinyl acetate (EVA-28) which is a commonly used resin for wire and cable insulation (Durin-France, 2000). The LDH was pre-dried at 70°C for 24 h in order to remove any surface water present which may have an adverse effect on the insulating and mechanical properties of the resin (Boggs and Xu, 2001, and references therein); interlayer water is held more strongly and less likely to give rise to problems. The resin was combined with LDH to give a composition of 60 wt.% LDH and mixed at a temperature of 140°C in a roller mixer. The EVA is known to be stable to degradation at these temperatures (see below). Two key fire-retardant properties are given in Table 1. The limiting oxygen index (LOI) value represents the minimum concentration of oxygen (expressed as percent by volume) in a mixture of oxygen and nitrogen that will support flaming combustion of a material that is initially at room temperature. The LOI values for the LDH-containing resins are comparable with and greater than that of the pure resin, indicating that addition of the LDHs has reduced the flammability of the material. Most noteworthy, however, is that whilst addition of the LDH-carbonate leads to a reduction in smoke density, the borate-pillared LDH has significantly better smoke-suppressing properties. The smoke density of the borate-pillared LDH/EVA composite is 45% less than that of the pure resin. In order to investigate the origin of the flame-retardant effects, some further experiments were carried out.

The TG curves obtained under dry air flow for pure EVA and its composites (60 wt.%) with the LDH-carbonate precursor and the borate-pillared LDH are shown in Figure 5 in which EVA itself is shown to decompose in a two-stage process. The first weight loss (320–350°C) has been attributed (Carpentier *et al.*, 2000b; Hull *et al.*, 2003) to the loss of acetic acid by β -elimination resulting in the formation of unsaturated

Table 1. Flame-retardant properties of different LDH fillers (60 wt.%) in composites with EVA-28.

Filler	Limiting oxygen index (%)	Smoke density
None	21.3	187.4
LDH- CO_3	30.0	133.1
LDH-borate	29.2	102.9

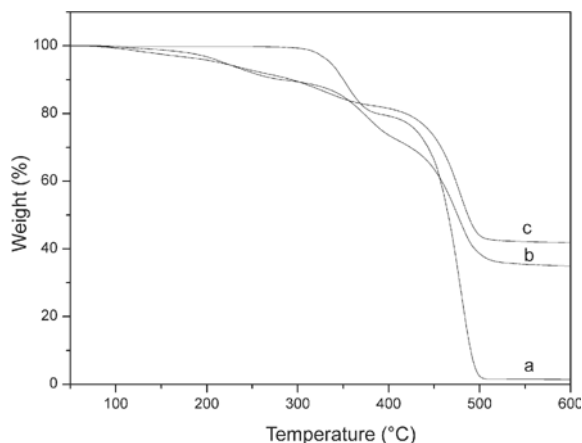


Figure 5. TG curves obtained under dry air flow for (a) pure EVA and its composite (60 wt.%) with (b) the Mg-Al LDH carbonate precursor and (c) the borate-pillared LDH. The presence of the LDH additives leads to a slight increase in the thermal stability of the polymer.

polyenes. The second step (425–500°C) involves degradation of the resulting hydrocarbon chains. In the case of the composites (Figure 5b,c), comparison with Figures 3 and 5a, suggests that the weight loss below 300°C is due to loss of water from the LDH, that between 350 and 450°C is due to decomposition of both LDH and EVA, whilst that above 450°C is mainly due to decomposition of the polymer. The presence of the LDH additives leads to a slight increase in the thermal stability of the polymer in this temperature range, particularly in the case of the borate-pillared LDH (Figure 5c). Similar results have been observed for EVA-Mg(OH)₂ flame-retardant formulations (Carpentier *et al.*, 2000b). The composition of the vapors emitted during the TGA process for the three materials was investigated by *in situ* mass spectrometry. For pure EVA, a large number of organic fragments with *m/z* (relative mass/charge ratio) >50 were observed, which were absent in the case of both LDH-EVA composites. This is consistent with the lower smoke densities observed during combustion of these materials.

Scanning electron microscope (SEM) images of the composites of EVA with the LDH-carbonate and the borate-pillared LDH after heating in air at 700°C are shown in Figure 6a and 6b, respectively. Comparison of the two micrographs clearly indicates that the LDH-borate forms a more complete protective layer which has been suggested (Carpentier *et al.*, 2000a, 2001) to be the basis of the smoke-inhibiting action of flame retardants. The powder XRD patterns of the composites of EVA with the LDH-carbonate and the borate-pillared LDH before heating (Figures 7a and 7c, respectively) are virtually identical to those of the respective LDH phases (Figure 1a,b) indicating that dispersion in the polymer has not disrupted the layer structure of the LDHs. After heating at 700°C, the LDH-carbonate composite decomposed to give a material with an XRD pattern

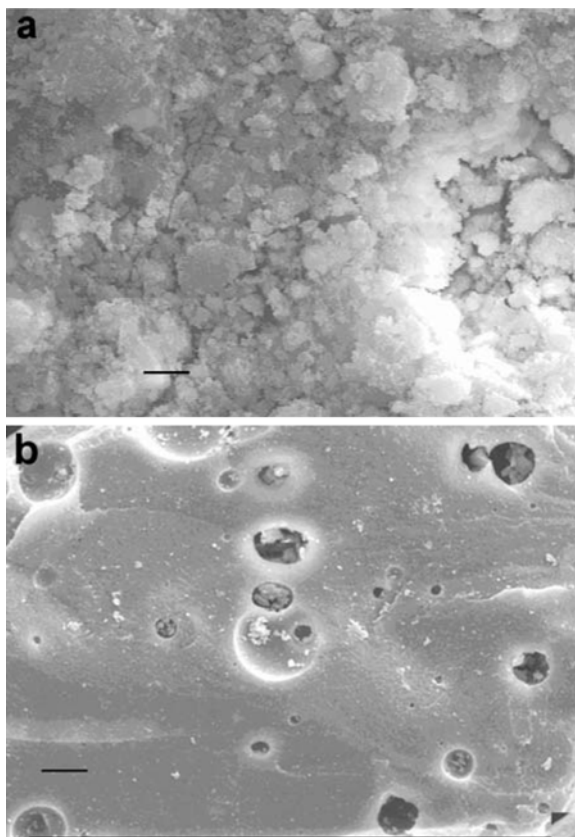


Figure 6. SEM images of the composites of EVA with (a) the Mg-Al LDH carbonate and (b) the borate-pillared LDH after heating in air at 700°C. The scale bar is 10 μm long. The LDH-borate forms a more complete protective layer which is probably responsible for its enhanced smoke-inhibiting properties.

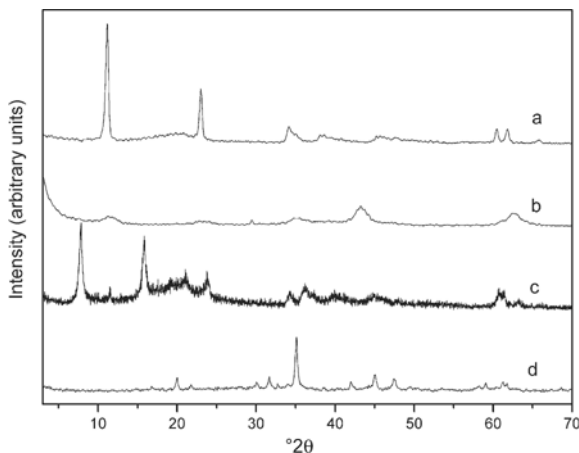


Figure 7. Powder XRD patterns of the composites of EVA with the Mg-Al LDH carbonate as prepared (a), after heating at 700°C (b), with the borate-pillared LDH as prepared (c), and after heating at 700°C (d). After heating, the Mg-Al LDH carbonate decomposes to give a material with an XRD pattern corresponding to that of a poorly crystalline MgO phase whilst the borate-pillared LDH decomposes to give a material with a diffraction pattern corresponding to that of fairly well crystalline Mg₂B₂O₅.

(Figure 7b) corresponding to that of a poorly crystalline MgO phase (JCPDS 4-0829), as is well known for such LDHs in the absence of polymer (Cavani *et al.*, 1991). In contrast, however, the material produced by decomposition of the LDH-borate composite has a diffraction pattern (Figure 7d) corresponding to that of fairly well crystalline $\text{Mg}_2\text{B}_2\text{O}_5$ (JCPDS 86-0531) (Guo *et al.*, 1995). Clearly, other amorphous phases such as Al_2O_3 , B_2O_3 or AlBO_3 must also be present, but on the basis of the stoichiometry of the LDH-borate precursor given above, the crystalline $\text{Mg}_2\text{B}_2\text{O}_5$ phase can be estimated to comprise ~60% of the calcined inorganic mixture and can be expected make a major contribution to the flame-retardant and smoke-inhibiting effects.

CONCLUSIONS

We have demonstrated that a borate-pillared LDH may be prepared by a simple procedure involving reaction of boric acid with an LDH in carbonate form. This LDH may be prepared very economically on a large scale (Duan and Jiao, 2000), so that large-scale production of the borate-pillared material is a viable proposition. The interlayer region contains polymeric triborate anions of the type $[\text{B}_3\text{O}_4(\text{OH})_2]_n^-$ with $-\text{B}-\text{O}-\text{B}-$ chains of BO_4 units oriented parallel to the layers, with each BO_4 unit forming a hexagonal B_3O_3 ring with two BO_3 units; these rings are probably oriented perpendicular to the layers. This is the first time that such anions have been confirmed as the guest species in LDHs. When used as a flame retardant with PVA, the synergistic effect between the borate anions uniformly distributed in the interlayer region and the host layers gives rise to enhanced smoke-suppressing properties compared to the LDH-carbonate precursor without compromising the flammability of the material. In practice, commercial formulations for cable insulation contain a number of components apart from the resin and flame retardant/filler and an optimization of the composition for materials containing borate-pillared LDHs is currently underway.

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