



## Research paper

## Effect of clay minerals structure on the polymer flame retardancy intumescent process



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## ABSTRACT

This study aimed at investigating the influence of the crystalline structure of a series of clay minerals on the flame retardancy of ethylene based polymer materials with and without an intumescent formulation. The clay minerals tested were mica, kaolinite (Kaol) and palygorskite (Pal). K-feldspar (K-Fsp) was also tested. The intumescent formulation used was composed of ammonium polyphosphate (APP) and pentaerythritol (PER). The flammability was evaluated using UL-94 classification, limiting oxygen index (LOI) and cone calorimeter analyses. The addition of Pal to the intumescent formulation led to the highest LOI value and a rate of heat release (RHR) close to zero, indicating that a great synergy occurred from the interaction of this clay mineral crystalline structure with the polymer chains and the intumescent formulation. The K-Fsp showed the lowest performance. The TGA and heating microscopy analyses showed that the addition of mica, Kaol or Pal led to the formation of a more thermally stable intumescent layer, and the crystalline structure of the clay minerals' appears to affect the synergy with APP/PER. The presence of the tetrahedral SiO<sub>4</sub> sheets on both sides of the interlayer space, as in the mica structure, or in the internal face of the channels, as in the Pal, seems to lead to a greater synergistic action.

## 1. Introduction

In the development of flame retardant polymeric materials, the use of clay minerals, other than montmorillonite (Mt), is less common. Some authors mention the addition of sepiolite in order to increase the flame retardant properties of polymeric matrices (Bourbigot and Duquesne, 2007). Batistella et al. (2015) showed that the flammability is sensitive to kaolinite (Kaol) particle dispersion and distribution in a polyamide matrix. Vahabi et al. (2012) prepared Kaol poly(methyl metacrylate) nanocomposites and demonstrated that the clay polymer nanocomposite (CPN) morphology influenced the peak rate of heat release (PRHR). Some researchers have shown that Mt. can catalyse the formation of a carbonaceous layer rich in aluminosilicates on the materials surface during combustion, reducing the rate of heat release (RHR) (Gilman, 1999; Wang et al., 2002; Qin et al., 2005; Hao et al., 2006; Lewin, 2006; Kiliaris and Pappaspyrides, 2010). However, it has been observed that the sole addition of clay minerals does not lead to

satisfactory flame retardant properties when considering, for example, parameters such as the LOI (limiting oxygen index) and UL-94 (Tang et al., 2002; Qin et al., 2005). Thus, many authors have suggested the concomitant use of conventional clay minerals and flame retardants, such as the intumescent formulation (Bartholmai and Schartel, 2004; Berta et al., 2006; Schartel et al., 2006; Hull and Stec, 2009; Tang et al., 2016; Dzulkafli et al., 2017). Generally, the intumescent formulations are composed of three ingredients: an acid source, a carbonaceous compound and a blowing agent. The mixture of these additives, when submitted to heat, form a carbonaceous layer, named char, which prevents the transfer of heat, fuel and oxygen, therefore extinguishing the flame (Beyer, 2005; Alongi et al., 2015; Dzulkafli et al., 2017). During this work, ammonium polyphosphate (APP) was used both as the acid source and the blowing agent, and pentaerythritol (PER) as the carbonaceous source. It has been demonstrated that the sole use of an intumescent formulation does not lead to satisfactory flame retardant properties, and that the sodic and organophilic Mt. can behave as

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synergic agents in a poly (ethylene-co-butyl acrylate) matrix containing an intumescent formulation of APP and PER (Ribeiro et al., 2008, 2011). Besides, it was also observed that the increase of the basal space of the Mt. affects the synergic action, decreasing both the LOI values and the UL-94 classification and therefore reducing the flame retardant properties of the polymeric material (Ribeiro et al., 2008, 2017).

The formation of the intumescent layer involves many steps. Initially, at temperatures below 280 °C, a mixture of esters is formed by the reaction of acid species generated by the degradation of APP and the carbonific agent PER. Next, the carbonization process occurs through the formation of double bonds, generated by the thermal degradation of the esters formed in the previous step, followed by Diels-Alder reactions (Bourbigot and Duquesne, 2007). Mt. can act as catalysts in the Diels-Alder and esterification reactions, which can contribute to the formation of char (Adams et al., 1994; Ribeiro et al., 2013). Furthermore, it has been also observed that the interlayer space of clay minerals has an important role in the catalysis of many chemical reactions. Alkenes, for example, are protonated in the interlayer of Mt., generating carbocation intermediates (Weiss, 1981; Laszlo, 1987). These results suggest that it would be interesting to investigate other features of the clay minerals crystalline structure that could have an influence on the process.

The objective of the present work was to evaluate the effect of different crystalline structures, as the ones present in clay minerals such as mica, Kaol, palygorskite (Pal), besides the K-feldspar (K-Fsp), on the fire retardance performance of the intumescent formulation. Depending on the results, new and more efficient synergic agents could be found, besides Mt., thus increasing the range of materials that could be used to improve the flame retardant properties of CPN.

## 2. Materials and methods

### 2.1. Materials and sample processing

The polymeric matrix used was poly (ethylene-co-butyl acrylate), supplied by Arkema, under the trade name of Lotryl 30BA02, here referred to as EBA-30. The intumescent formulation was composed by ammonium polyphosphate (APP), supplied by Clariant under the trade name Exolit 422 and pentaerythritol (PER) acquired from Sigma – Aldrich. The samples produced contained 30 wt% of the APP:PER intumescent formulation, mixed in the proportion of 3:1, in which case, according to the literature, maximum flame retardant properties are observed for polyethylene based materials (Bourbigot et al., 1996). Kaol, Pal, K-Fsp and mica mineral were all supplied by UBM – *União Brasileira de Mineração*. With the exception of the mica, supplied in laminar form, all the other minerals were supplied as powder, and because of this, the mica had to be previously milled with mortar and pestle before being introduced in a Pulverisette 14 mill model at 10,000 RPM in order to be added to the polymer. All the materials were dried for 14 h at 70 °C before being processed with the polymeric material. The clay minerals were added to compose 3% of the total mass of the polymeric mixture, since, according to Estevão et al. (2004) the maximum flame retardant properties are observed at this concentration.

The following materials: raw EBA-30, EBA-30 + Kaol (3%), EBA-30 + Pal (3%), EBA-30 + mica (3%), EBA-30 + K-Fsp (3%), EBA-30 + APP/PER (3%), EBA-30 + APP/PER + Kaol (3%), EBA-30 + APP/PER + Pal (3%), EBA-30 + APP/PER + mica (3%), EBA-30 + APP/PER + K-Fsp (3%) were processed using a Haake Rheocord 9000 internal mixer with a Rheomix 600 chamber. The rotors used were of the Roller Blades type and the mixtures were produced at 140 °C and under 50 RPM. The polymer was firstly introduced in the heating chamber and, after 5 min, the additives were added, being mixed during an additional period of 10 min. The material was then pressed at 150 °C in a Carver press with a total load of 9000 kgf on a 10 × 10 cm area, in order to obtain 3 mm thick specimens, which were then used to obtain all of the test samples.

### 2.2. Characterization

The clay minerals, K-Fsp and all the polymeric materials produced were characterized using a Perkin-Elmer 7 high temperature thermogravimetric analyser (TGA). The analysis was performed using a 10 mg sample in platinum capsules under a heating rate of 10 °C/min varying from 30 °C to 850 °C. Synthetic air was used as the purge gas with a 20 mL/min flux.

A Micromeritics, model ASAP 2010 (Accelerated Surface Area and Porosimetry), was used for the textural analysis. It measures the samples specific area using the B.E.T. (Brunauer – Emmet – Teller) method, through N<sub>2</sub> adsorption and desorption isothermals at 77 K. The clay minerals were dried beforehand in a furnace at 80 °C during 16 h. Inside the ASAP equipment, the sample was pre-treated under vacuum at the aforementioned drying temperatures up to a 2 μm Hg/min minimum degassing rate.

The clay minerals and K-Fsp particle sizes were obtained using a Malvern Instruments, model Mastersizer 2000 particle analyser, whose measurements are based on light diffraction. The equipment holds a 200 mL capacity container where the samples are suspended in water and stirred by a rotor at 300 RPM. Ultrasound is applied to increase particle dispersion in the medium.

The qualitative determination of the minerals presents in the Pal, mica, K-Fsp and Kaol samples was carried through X-ray diffraction (XRD). The samples' XRD pattern, obtained by the powder method, were collected by a Bruker-AXS D8 Advance Eco equipment using the following operation conditions: radiation Cu Kα (35 kV/40 mA); goniometer speed of 0.02° 2θ per step with a time count of 1 s per step and collected from 5 to 80° 2θ. The qualitative interpretation of the X-ray diffraction patterns were carried out by comparison with the pattern contained in the PDF02-ICDD2006 database from the Bruker Diffrac Plus software.

For the materials' flammability evaluation, LOI, UL-94 classification and cone calorimeter techniques were used. The LOI tests standardized (ISO 4589-2) and allows the determination of the minimum oxygen content necessary to sustain the burning process in an oxygen and nitrogen gas mixture atmosphere. For this test, an FTT instrument was employed with 100 × 6.7 × 3 mm samples, following the procedure described in the ISO 4589-2 standard. The UL-94 classification measures the ignitibility of the materials. The material is rated according to its burning characteristics and the time necessary to extinguish the flame after it has been removed. The highest rating is V0, where the material rapidly extinguishes the flame and does not produces burning drips. The cone calorimetry is considered the technique which best reproduces fire conditions in a laboratory scale experiment. Through cone calorimetry it is possible to obtain a quantitative measurement of the rate of heat release – RHR (expressed in KW/m<sup>2</sup>), taken as the analysis' most important parameter (Babrauskas and Peacock, 1992; Gilman, 1999). The analyses were performed in triplicates using a mass loss cone calorimeter MLCC, model FTT-0014/2012 according to the ISO 5660-1 (2002) standard. Specimens of 100 × 100 × 3 mm were irradiated in horizontal position with a 50 KW/m<sup>2</sup> heat flux, which corresponds to the heat released during well developed fires (Schartel et al., 2005). Intumescence can be monitored *in situ* through heating microscopy (Estevão and Nascimento, 2002). This technique allows the visualization of the samples behavior under heating and the integrity of the intumescent layer structure at high temperatures. The heating microscopy analyses were carried out with a Leitz heating microscope, model 1A, and the images were captured by a Samsung SDC 415 ND camera. The samples used were 3 mm sided cubes.

## 3. Results and discussion

### 3.1. Characterization

The TGA curves for the clay minerals and K-Fsp are shown in Fig. 1.

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