Applied Clay Science 143 (2017) 399–407

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Glow-wire evaluation of polymeric materials for the electric sector: Effect of the interlayer spacing of montmorillonite

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ARTICLE INFO

Keywords:
Intumescent formulation
Glow-wire
Interlayer spacings
Montmorillonites
Flame retardant

ABSTRACT

In this study the glow-wire technique was used in the evaluation of synergistic effects between organophilic montmorillonites with different basal spacings and an intumescent formulation containing ammonium polyphosphate (APP) and pentaerythritol (PER) in a poly (ethylene-*co*-butyl acrylate), EBA 30, polymeric matrix. The flammability of the samples was also evaluated through limiting oxygen index (LOI) analyses, UL-94 standard rating and heating microscopy. The morphology of the samples was studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD). These analyses revealed that processing in a twin screw extruder led to the formation of intercalated and exfoliated nanocomposites. The influence of processing *via* internal mixer and twin-screw extruder was also evaluated. Glow-wire tests revealed that the addition of montmorillonites with smaller basal spacings led to a synergistic effect with the intumescent formulation, an effect which was not observed when using montmorillonites with basal spacings larger than 30 Å. The intumescent materials containing montmorillonites with smaller basal spacings showed GWFI (glow-wire flammability index) as high as 960 °C, which indicates that they could be used in the electrical area.

1. Introduction

The use of polymeric materials with flame retardant properties has been a requirement in the electricity sector of the industry. In this regard, the glow-wire technique becomes an important test as it allows for the evaluation of flame retardant properties of materials designed to be used in the sector (Guillaume et al., 2011).

There are very few studies in the literature that report measurements related to the use of the glow-wire. Some studies do show the technique being used in the evaluation of polymer nanocomposites containing organophilic clays (Shah et al., 2009; Modesti et al., 2006; Acquasanta et al., 2011). However, these clay-polymer nanocomposites, despite having a higher thermal stability than the pure polymer, do not reach satisfactory values of LOI (limiting oxygen index) or UL-94 classification (Vertical Burning), which are standard tests for evaluating the fire retardance of polymers (Kiliares and Papaspyrides, 2010). Therefore, alternatives have been sought to improve the fire performance of these nanocomposites, such as the concomitant use of clay minerals and intumescent systems.

Generally, an intumescent formulation contains three components: an acid source, a carbonaceous compound, and a blowing agent. Under heating, these additives form a carbonaceous tumid layer called char, which prevents heat, fuel and oxygen transfer, hence extinguishing the flame (Jimenez et al., 2006; Bourbigot and Le Bras, 1998). In the present study ammonium polyphosphate (APP) was used as an acid source and a blowing agent, and pentaerythritol (PER) was added as a carbonific source. However, it has been observed that the sole use of the intumescent formulation does not lead to suitable flame retardant properties, such as those registered through LOI testing and UL-94 ratings. Thus, additives such as natural and organophilic montmorillonites have been used by our research group as synergistic agents (Ribeiro et al., 2008; Ribeiro et al., 2011) in intumescent formulations in order to overcome this problem. Moreover, there are very few studies that use the glow wire technique in evaluating polymeric materials containing an intumescent formulation and synergistic agents (Schartel et al., 2003; Jimenez et al., 2013; Horrocks et al., 2014; Naik et al., 2013), making it still an underexplored technique.

This study aimed at evaluating the potential of the glow-wire technique for the characterization of the synergistic action between montmorillonites and an intumescent formulation composed of APP

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http://dx.doi.org/10.1016/j.clay.2017.04.018
Received 20 July 2016; Received in revised form 13 April 2017; Accepted 15 April 2017

and PER as well as in determining the influence of the montmorillonite's interlayer spacings on this synergy, a phenomenon that has already been observed through other techniques, such as LOI, UL-94 and cone calorimeter (Ribeiro et al., 2011; Ribeiro et al., 2008). Additionally, since processing can have a strong influence on the material's morphology, the effect of the type of compounding process employed on the samples performance was also evaluated. This was accomplished by comparing the LOI and UL-94 results obtained for mixtures produced in a twin screw extruder with the results already reported by our group for samples produced in an internal mixer (Ribeiro et al., 2008; Ribeiro et al., 2013). Images are presented obtained with heating microscopy of the materials. These images permit *in situ* monitoring of the char swelling during the heating process. Finally, the potential use of the developed materials in the electricity sector was evaluated.

2. Materials and methods

2.1. Materials and sample processing

The polymer matrix used was a poly[ethylene (30%)-butyl acrylate] copolymer supplied by Elf-Atochem under the trade name Lotryl 30BA02, hereafter referred to as EBA-30. The intumescent formulation used was composed of ammonium polyphosphate (APP), supplied by Clariant under the trade name Exolit 422, and pentaerythritol (PER), purchased from Sigma-Aldrich. For the polymer blends produced, the intumescent formulation represented 30 mass% of the total mass, with a 3:1 ratio of APP:PER, which according to the literature, is the ratio in which the best flame retardancy properties are observed for the polyethylene-based materials (Bourbigot et al., 1996). The sodic montmorillonite and the two organophilic montmorillonites used were provided by Southern Clays under the trade names Cloisite Na, Cloisite 30B and Cloisite 15A, respectively. The clays were characterized by different methods. The chemical composition was determined by X-ray fluorescence analysis using a Rigaku RIX 3100 X-ray spectrophotometer and the particle size distribution was determined in a Malvern Mastersizer 2000 analyzer. Textural analysis was carried out using a Micromeritics analyzer (ASAP 2010), through which the specific surface area was obtained.

The following materials were evaluated: EBA-30 (pure), EBA-30 + Cloisite Na (3%), EBA-30 + Cloisite 30B (3%), EBA-30 + Cloisite 15A (3%), EBA-30 + APP/PER + Cloisite Na (3%), EBA-30 + APP/PER + Cloisite 30B (3%) e EBA-30 + APP/PER + Cloisite 15A (3%).

All the polymers were processed in a TeckTrill DCT-20 twin screw extruder with nine heating zones which were maintained at the following temperatures: Tzone 1 = 160 °C, Tzone 2 = 165 °C, Tzone 3 = 165 °C, Tzone 4 = 170 °C, Tzone 5 = 170 °C, Tzone 6 = 170 °C, Tzone 7 = 175 °C, Tzone 8 = 175 °C and Tzone 9 = 175 °C. The head temperature was maintained at 180 °C. The physical mixture of the polymer and additives was fed into zone 1, at an overall rate of 5 kg/h, using rotation of 11 rpm and screw speed of 300 rpm. After extrusion, the materials were passed through a Brabender pelletizer. Moreover, the systems containing only the polymer and Cloisites, without the intumescent formulation, were also processed in an internal mixer. These samples were mixed in a Haake Rheocord 9000 rheometer, equipped with a rheomix chamber 600 and roller blades rotor, at 160 °C under 50 rpm for 15 min. After both processes the samples were then pressed in a Carver press at 150 °C with an applied load of 9000 kg on a 100 mm × 100 mm area, in order to obtain sheets 3 mm thick, from which all test samples were produced.

2.2. Characterization

The morphologic characterization of the materials was performed by X-ray diffraction (XRD) analysis and, for this purpose, the samples studied were previously pulverized in a Fritsh Pulverisette 14 cryogenic mill, at 10,000 RPM, for better homogenization. The analyses were performed in a Rigaku Miniflex X-ray diffraction instrument with a copper anode, operating voltage of 30 kV and filament current of 15 mA. Scanning was carried out in a rate of 0.05°/s, from 2° to 30° (2θ).

In addition to the XRD analysis, transmission electron microscopy analysis (TEM) was also used to evaluate the morphology. The samples were previously cooled to − 140 °C and cut into slices 60 nm thick with a diamond knife in a Leica Ultra cut Richert 5 ultramicrotome. The histological sections were collected on 400 mesh copper grids, and analyzed by a Zeiss Libra 120 transmission electron microscope operating with a voltage of 80 kV. The images were obtained with a Cantega 2 K Olympus camera and with the iTEM acquisition platform. Due to the considerable hardness of samples containing APP/PER, these were not analyzed by TEM, as they could damage the diamond knives of the ultramicrotome.

LOI, UL-94 and glow-wire techniques were used to evaluate the flammability of the materials produced. The LOI analyses were carried out in an FTT instrument with samples measuring 100 mm × 6.7 mm × 3 mm, following the procedure described in the ISO 4589-2 standard. The samples were rated by the UL-94 test, according to the ANSI/ASTM D 635-77 standard.

The glow-wire technique is a test employed for assessing the flammability of polymeric materials used in the electrotechnical industry (Guillaume et al., 2011). During the test, a glowing tip, heated to a certain temperature, comes into contact with the specimen, simulating a thermal stress. This type of stress could be generated in electrotechnical systems due to inadequate installations or overload in its subassemblies and components. A CEAST 6447A instrument was used for the glow-wire tests. This equipment allows the contact, for 30 s, of an incandescent tip, heated by an electrical resistance under the conditions specified in IEC 60695-2-10 standard (International Electrotechnical Commission, part 2-10, 2000a,b).

Two different tests can be performed by a glow-wire instrument. In the first test, described by IEC 60695-2-10 and IEC 60695-2-12 standards, the instrument is set at a temperature between 550 and 960 °C (550, 600, 650, 700, 750, 800, 850, 900 or 960 °C) which will promote the glowing of the tip of the equipment. After the stabilization of the temperature, the tip comes into contact with a sample with dimensions of 70 mm × 70 mm × 3 mm. During the application of the glowing tip, and for another 30 s after its removal, the specimen and the paper positioned below the sample must be observed. After the test, the result is considered satisfactory if ignition of the specimen does not occur (ignition is characterized by a flame that remains visible for more than 5 s). The test is also considered satisfactory if both of the following conditions are fulfilled: (a) the flame or glowing is extinguished within 30 s after the removal of the glowing tip; (b) there is no ignition, through dripping, of the paper positioned below the specimen. Thus, the GWFI (Glow-Wire Flammability Index) is defined as the highest test temperature at which these conditions are fully achieved within three consecutive tests (International Electrotechnical Commission, part 2-10, 2000a,b).

The second test conducted with the glow-wire equipment is for determining the GWIT (Glow-Wire Ignition Temperature). The GWIT is calculated by adding 25 °C to the highest temperature tested at which ignition of the specimen does not occur in three consecutive tests. The specimen dimensions are the same as those described for the GWFI. The method of analysis and the definition of the GWIT are described in the IEC 60695-2-12 standard.

The samples were further characterized by heating microscopy. This technique allows visualization of the formation and maintenance of the intumescent layer during heating, and has been very useful for *in situ* monitoring of char formation (Ribeiro et al., 2011; Estevao and Nascimento, 2002). The analyses were performed in a Leitz heating microscope, model 1A, under a heating rate of 40 °C/min using 3 mm side cubic samples.