



A comprehensive study of the synergistic flame retardant mechanisms of halloysite in intumescent polypropylene



B. Lecouvet^a, M. Sclavons^a, C. Bailly^a, S. Bourbigot^{b,*}

^aBio- and Soft Matter (BSMA), Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain (UCL), Croix du Sud 1, Box L7.04.02, B-1348 Louvain-la-Neuve, Belgium

^bUnité Matériaux et Transformations, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), 59652 Villeneuve d'Ascq, France

ARTICLE INFO

Article history:

Received 4 June 2013

Received in revised form

12 August 2013

Accepted 16 August 2013

Available online 29 August 2013

Keywords:

Halloysite

Ammonium polyphosphate

Polypropylene

Flame retardancy

Synergy

ABSTRACT

This work aims to evaluate the efficiency of halloysite as synergistic agent in an intumescent PP system based on a coated ammonium polyphosphate (IFR). The first part of the study analyses the thermal stability and fire performance of PP when using the intumescent formulation alone or in combination with the aluminosilicate nanotubes (HNTs). Cone calorimetry reveals that partial substitution of IFR by HNTs (3 wt.%) imparts substantial improvement in flame retardancy with reduced heat release rate and longer burning times. Additionally, a shift from V-1 to V-0 classification is achieved at the UL-94 test with only 1.5 wt.% HNTs. The second part provides a better understanding of the physical and chemical mechanisms of action of HNTs in the intumescent systems. The chemical evolution of the condensed phase during combustion is described by solid state NMR, and in particular using 2D NMR. Results indicate that halloysite speeds up the development of the intumescent shield, but also enhances its mechanical properties by physical reinforcement (i.e. aluminosilicate “skeleton-frame” for the phospho-carbonaceous structure) and/or by chemical interactions with IFR yielding to aluminophosphates. These new chemical species allow thermal stabilization of the char at high temperatures and provide good macro- and micro-structural properties. Both effects increase the mechanical strength of the protective layer during burning ensuring excellent heat and mass transfer limitations between gas and condensed phases.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, polymeric materials are massively used in our everyday life thanks to their remarkable combination of properties. However, many synthetic polymers are easily flammable due to their organic nature, with some of them producing huge amount of toxic gases and smoke during the combustion process [1]. The incorporation of flame retardant additives has proved to be an effective way to reduce their flammability [2]. Halogenated flame retardants have been first considered to reinforce the fire retardancy of polymers by means of a gas-phase action [3]. However, their use is increasingly contested due to the potential toxicity of the decomposition products such as halogen acids and metal halides [2,4], as well as their persistency in the environment and bioaccumulation. Moreover, some halogenated compounds can also cause damage to immune and endocrine systems [5,6]. Therefore, the general trend is to substitute these flame retardants by non-halogenated alternatives.

Recently, much attention has been devoted to the use of nanoparticles (e.g. clay, carbon nanotubes, polyhedral oligomeric silsesquioxane (POSS), etc.) [7–12]. Numerous studies have reported large reduction of the heat release rate (HRR) with prolonged combustion time for polymer-clay nanocomposites in cone calorimetry [7,13,14]. As an example, it has been shown in a previous work that the addition of well-dispersed halloysite nanotubes (HNTs) in PP can significantly reduce the HRR, with a decrease in the peak value of 65% at clay concentration of 16 wt.% [15]. The most popularly accepted mechanism to explain the fire retardancy of polymer-clay nanocomposites is based on barrier effects [13,16]. The incorporation of a relatively low amount of nanoclay in a polymer matrix enables the formation of a protective inorganic-rich layer at the sample surface during combustion thanks to a combination of ablative reassembling and migration of the nanoparticles [17,18]. The physical barrier reduces heat and mass transfer between gas and condensed phases, with consequent lower flame intensity (i.e. HRR).

However, although this condensed-phase mechanism can strongly reduce the flame spread, other important fire parameters are not improved in any relevant way: the time to ignition (TTI) of

* Corresponding author. Tel.: +33 (0)3 20 43 48 88.

E-mail address: serge.bourbigot@ensc-lille.fr (S. Bourbigot).

clay-based composites is almost always shorter than that of neat polymer [14,15,19,20] and the relative decrease in the total heat released (THR) is commonly of the same order of magnitude as the inorganic content in the matrix [13,15,16,21]. Therefore, the protective layer only slows down the burning process without decreasing the total amount of combustible materials [22]. Furthermore, these flame retardant systems fail other important fire testing methods, in particular those with samples tested in vertical position such as UL-94 rating and limiting oxygen index (LOI) [23]. In view of these limitations, nanoclay (and nanoparticles in general) should be preferably regarded as a part of flame retardant formulations, instead of stand-alone flame retardants.

Among halogen-free fire retardants, intumescent additives have been found to be suitable for the development of fire safe polymers. An intumescent formulation is defined as a flame retardant system which, when heated beyond a critical temperature, begins to char and swell, yielding to the formation of a foamed cellular carbonaceous layer on the outer surface of the burning material [24]. The intumescent structure shields the substrate from the external heat exposure and the heat feedback from the flame. It also impedes the transport of oxygen and flammable gases. Besides, dripping of the molten polymer is reduced by char formation, eliminating a possible source of further flame spread. In general, intumescent flame retardant (IFR) systems contain three ingredients [25]: (i) an acid source (e.g. ammonium polyphosphate (APP)) which triggers the dehydration of the char former; (ii) a carbonization agent (e.g. polyol) charring upon reaction with the mineral acid; and (iii) a blowing agent (e.g. melamine) which enables the char expansion through the release of inert volatile species. The insulating properties of the intumescent coating are influenced by its mechanical and thermal stability under severe conditions [26]. Indeed, the external environment and the internal pressure exerted by the decomposition products can lead to crack formation and propagation in the intumescent structure, decreasing its barrier efficiency. Moreover, the heat transport by convection and radiation is also strongly affected by the morphology of the cells in the intumescent layer (size, open/closed cell foam). For that reason, additional ingredients (e.g. mineral oxides, zeolites, etc.) can be incorporated into polymer intumescent systems to reinforce the mechanical and thermal properties of the protective layer either by physical and/or chemical synergistic effects.

Among the wide variety of flame retardant additives, clay nanoparticles have been identified as promising synergistic agents when combined with polymer intumescent systems [27–30]. As an example, Bourbigot et al. studied the mechanical and fire behaviour of an EVA/(APP/PA6) intumescent system when replacing neat PA6 (i.e. carbonization agent) by PA6-clay nanocomposite containing 2 wt.% exfoliated MMT [31]. As expected, the highest mechanical reinforcement was observed in presence of the nanoclay. Interestingly, the incorporation of aluminosilicates in PA6 further reduced the pHR from 320 to 240 kW/m² and the final residue appeared more rigid and less cracked than that without clay. The chemical action of MMT was investigated by solid state NMR and revealed the formation of aluminophosphates in the condensed phase because of chemical reactions between APP and clay, leading to a thermal stabilization of the phosphorocarbonaceous structure at high temperatures. The addition of clay also improved the ignitability and self-extinguishing behaviour of the EVA intumescent formulation; LOI increased from 32 to 37 vol.% and V-0 rating was achieved at lower APP concentration (10 instead of 13.5 wt.%).

Lu and Wilkie compared the synergistic effect of different additives (organoclay, CNTs, iron oxide and nickel catalyst) on the flame retardancy of APP/TPE (tripentaerythritol) intumescent polystyrene systems [32]. The largest decrease in pHR combined

with longest combustion time was observed when IFR was partially substituted by MMT. This observation was correlated to the highest expansion rate of the intumescent-clay coating and its stronger and more cohesive pillared “top-bottom” structure made of multicellular foam.

The melt viscosity of the condensed phase is also a key parameter controlling the swelling process of the intumescent structure. Isitman and Kaynak compared the synergistic action of two nanofillers (nanoclay vs. CNTs) within a commercial intumescent formulation based on a mixture of aluminium diethyl phosphinate, melamine polyphosphate and zinc borate in a PMMA matrix [33]. The combination of IFR and intercalated clay gave the largest reduction in pHR, while well-dispersed CNTs led to a deterioration of the flame retardancy with increased heat release and mass loss rates. According to the authors, the percolated CNTs network significantly increases the melt viscosity of the intumescent system, and hence hinders its expansion leading to the formation of an unfoamed char with poor insulating properties. Similar conclusions have been reported in literature [30,32].

The ratio at which the different ingredients are present is also of utmost importance. Several studies have shown that the most effective intumescent systems are obtained when only a few percent of IFR is substituted by clay [34–37]. The presence of an optimum nanofiller fraction in the intumescent composition is explained by the dual role of clay in the fire protection [34]. Apart from its positive barrier effects, the ablative reassembling of nanoparticles can hinder the escape of inert gases that cause the char to swell, but also increase the melt viscosity. Therefore, above a certain clay concentration, the expansion rate and the final thickness of the char are reduced, leading to an antagonistic effect on the flame retardancy of the intumescent system.

In this context, the present study aims to investigate the potential synergistic action of halloysite nanotubes on the thermal stability and flammability performance of an intumescent polypropylene system based on ammonium polyphosphate. This paper is organized in two main sections. First, thermogravimetric analyses are carried out to reveal potential chemical interactions between the additives when combined together. The flammability measurements of the intumescent formulations, with and without clay, have been conducted using cone calorimeter and UL-94 tests and the char residues are completely described. Afterwards, a mechanism of action of halloysite is proposed to explain the thermal and mechanical stabilization of the foamed cellular charred layer. The beneficial effect of HNTs is examined by following simultaneously the temperature profile in the condensed phase and the expansion rate of the intumescent coating throughout the cone calorimeter test. Solid state NMR is also used to characterize the chemical composition of the intumescent char during combustion.

2. Experimental

2.1. Materials

A commercially available polypropylene (HH420FB) was purchased from Borealis (Belgium) and PP-graft-maleic anhydride (PP-g-MA) Polybond 3200 was provided by Chemtura (Belgium). A commercial grade of pristine halloysite was supplied by Sigma-Aldrich (Germany). The specific surface area of the aluminosilicate is 64 m²/g, cation exchange capacity is 8 meq/g, pore volume is 1.25 ml/g, and specific gravity is 2.53 g/cm³. The intumescent formulation, an ammonium polyphosphate (APP) derivative (Buditec 3167), was kindly provided by Budenheim (Germany). It is an APP coated with a component containing nitrogenous and carbonaceous species (22 (w/w)% P, 21 (w/w)% N, 0.1 (w/w)% water).

Download English Version:

<https://daneshyari.com/en/article/5202267>

Download Persian Version:

<https://daneshyari.com/article/5202267>

[Daneshyari.com](https://daneshyari.com)