



## Macromolecular Nanotechnology

## The synergistic effect of organically modified sepiolite in intumescent flame retardant polypropylene

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## ABSTRACT

The pyrolysis, flammability and fire behavior of polypropylene (PP) containing an intumescent flame retardant and sepiolite nanoparticles were investigated by performing thermogravimetry, oxygen index (LOI), UL-94, and cone calorimeter tests. The combination of 0.5 wt% of premodified sepiolite (OSEP) with 12 wt% of a commercial intumescent flame retardant showed a clear synergy in LOI, UL-94 ranking and peak heat release rate. The ternary formulation achieved a V-0 classification and, consequently, allowed a reduction in the amount of flame retardant necessary to achieve this result. Whereas OSEP and pristine sepiolite nanoparticles (SEP) affect the performance in PP nanocomposites quite similarly, OSEP outperformed SEP in the combination with intumescent flame retardant. The cone calorimeter results and dynamic rheological measurements confirmed the synergistic effect between the nanofiller and the flame retardant resulting from the improved properties of the residual protective layer.

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## 1. Introduction

Intumescent flame retardants are quite efficient, especially for polyolefines [1–3]. This kind of flame-retardant system consists of three components (acid source, carbonization agent and blowing agent) [4,5], whose aim is to produce a swollen char layer that provides a barrier against heat and mass transfer between the flame zone and the pyrolysis front within the polymeric material [6–8]. This particular mechanism suggests that it is really important to improve the protective effect to obtain a better degree of flame retardancy [9].

The main advantages of intumescent flame retardants are the low amount of toxic gases released during burning, the antidripping behavior, and the absence of halogens, whereas drawbacks are their low thermal stability and limited flame retardancy efficiency as compared to halogenated flame retardants. In order to get higher performance, new intumescent systems have been developed by the use of synergistic agents such as zeolites [10–12], polyhedral silsesquioxane [13], montmorillonite [14], organoboron siloxane [15,16] and metal oxides [17,18]. In recent years, the development of new polymer nanocomposite systems with enhanced flame behavior has attracted growing interest [19–23]. In these cases, the huge surface area of nanofillers allows significant improvements to be obtained in mechanical, optical, thermal, and flame retardancy

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properties. With specific reference to this latter aspect, various mechanisms have been proposed for nanocomposites materials as the formation of a residual carbonaceous-inorganic protective layer and/or the reinforcement of the char as well as changes in melt viscosity during [24–32].

In this frame, sepiolite is one of the most promising nanofillers [33–35]. It is a porous clay with the formula  $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$  and, unlike other clays, its particles have a nanometer-size tunnel structure and needle-like morphology. The high surface area and porosity as well as the unusual particle shape allow outstanding sorption capacity and colloidal properties to be achieved. Moreover, the high density of silanol groups is a key factor for adhesion and compatibility with polymeric materials [36–39].

Previous studies have focused on the synergistic effects between sepiolite or organically modified sepiolite and flame retardants like zinc borate in a polypropylene (PP) matrix [40].

Hapuarachchi et al. [41] investigated polypropylene/sepiolite/carbon nanotubes ternary systems prepared by melt compounding and observed that the peak of heat release rate (PHRR) is remarkably reduced by 82% with respect to the neat matrix in the cone calorimeter tests.

Gul et al. [42] reported on the synergistic effect on flame retardancy of sepiolite incorporated into a linear low density polyethylene (LLDPE)/magnesium hydroxide (MgOH) composite. Ternary systems reached a LOI value equal to 36.5%.

Huang et al. [43] considered melt compounded materials including sepiolite and an intumescent flame retardant in a polypropylene resin. Results demonstrated that sepiolite had a significant influence on the flame retardancy with a LOI value equal to 36.0% in presence of 1.0 wt% of sepiolite at the total amount of additives kept constant at 25 wt%.

However synergisms and, more in general, benefits on the fire behavior have been highlighted not only for thermoplastic composites but also for systems based on thermosetting matrices for which catalytic and/or reinforcing char effects have been demonstrated. For example, Hapuarachchi et al. [44] confirmed these considerations for ternary nanocomposites based on unsaturated polyesters. Zotti et al. [45], instead, analyzed the influence of as received and dehydrated sepiolite clays on the fire behavior of a commercial epoxy resin. They observed a significant reduction of the PHRR in presence of 10% by weight of sepiolite with respect to neat epoxy matrix. Moreover, morphological observations of the char surface after cone calorimetry tests, emphasized the presence of fractures more and more evident with the increase of the filler content. These effects were particularly pronounced for systems containing dehydrated sepiolite particles with respect to ones containing as received clays.

In this work, a commercial PP resin was modified adding an intumescent flame retardant (ET) and sepiolite clays by melt compounding. Main aim of the research was to study the influence of the combination of ET with as received or opportunely modified sepiolite clays, SEP or OSEP respectively, on the flammability and fire retardancy of PP based formulations.

## 2. Experimental

### 2.1. Materials and preparation of samples

PP (block copolymer propene-ethene, melt flow rate 25 g/10 min according to ISO 1133) used in this work was produced by Unipetrol under the trade name MA 524. The ET (trade name Exolit AP 766, ammonium polyphosphate as main component, 24% w/w phosphorus content, 15% w/w nitrogen content) was supplied by Clariant and used as received. Polybond 3200 (PB 3200, 1% w/w of maleic anhydride) was produced by Additivant. SEP was purchased from Sigma Aldrich, while the organically modified OSEP was prepared in laboratory according to the following procedure by He et al. [40]:

- 25 g SEP were poured in 240 mL of deionized water and mixed at room temperature. Hydrochloric acid (HCl) was added to the system to obtain a pH value equal to 3–4. The resulting slurry was stirred for 5 h at room temperature. Subsequently it was filtered using a Buchner funnel. Finally, the obtained material was dried overnight.
- 12 g of acid sepiolite were mixed with 180 mL of deionized water at room temperature. A second mixture of 10 wt% CTAB (cetyltrimethylammonium bromide) was prepared, after that 5.7 mL were added to the first suspension. The resulting mixture was stirred for 5 h at 75 °C, then filtered using a Buchner funnel and dried overnight to obtain OSEP.

PP-based formulations (Table 1) were prepared using an HAAKE PolyLab twin screw extruder employing the temperature profile 160–170–180–190–200–200–190–175–175 °C from the hopper to the die, and a screw speed equal to 60 rpm.

**Table 1**  
Composition of the materials.

Sample code	PP (wt%)	ET (wt%)	PB3200 (wt%)	SEP (wt%)	OSEP (wt%)
PP	100	–	–	–	–
PP/0.5SEP	99	–	0.5	0.5	–
PP/0.5OSEP	99.5	–	–	–	0.5
PP/12ET	88	12	–	–	–
PP/15ET	85	15	–	–	–
PP/12ET/0.5SEP	87	12	0.5	0.5	–
PP/12ET/0.5OSEP	87.5	12	–	–	0.5

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