



Fire retardancy of polypropylene/kaolinite composites



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ABSTRACT

In this study the influence of surface modification of kaolinite with trisilanolisooctyl Polyhedral Oligo-SilSesquioxane (POSS) in polypropylene composites was evaluated in terms of thermal stability and fire retardancy and compared with talc. Thermogravimetric analysis showed that incorporating 30 wt% of kaolinite enhanced the thermal stability by ca. 20 °C compared to neat polymer. Cone calorimeter results demonstrated that kaolinite can greatly reduce the pHRR but not unmodified kaolinite. Rheological measurements showed that surface treatment of kaolinite leads to a decrease in viscosity, which could enhance processability. Finally, a correlation between viscosity and pHRR was found and the fire behavior of PP containing modified kaolinite could be explained.

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1. Introduction

Kaolinite is a 1:1 aluminosilicate composed of two layers of an alumina like tetrahedral sheet and a silica like octahedral sheet with the formula: $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Kaolinite has many industrial applications because of its special characteristics: chemically inert in a wide pH range, great covering power [1] when used as a pigment or as a surface coating for painting applications, low thermal conductivity and a lower cost compared to some current mineral fillers used in polymers. Main uses of kaolinite are in paper and ceramic industries and few studies concern its use in polymers [2–7]. Recently, we [7] studied the fire retardancy of an ultrafine kaolinite in EVA composites and compared this kaolinite with aluminum trihydroxide (ATH). Results showed that EVA filled with kaolinite exhibited better performances in terms of pHRR compared to EVA/ATH composites.

Polypropylene (PP) is commonly used due to its attractive versatility in terms of properties and processability. Nevertheless, poor flame retardancy is the main drawback of PP. To reduce its flammability, several kinds of flame retardant additives such as

halogenated compounds, metal hydroxides, intumescent systems [8,9], and mineral fillers have been used [10–14]. Among these flame retardants, the use of hydrated mineral fillers presents some drawbacks because satisfactory flame retardant properties are only achieved at high loading levels (up to more than 60% wt) leading to adverse impact on processability and mechanical properties. Beyond ATH and MDH (magnesium dihydroxide), other additives have been studied in the literature [9,14–19]. Fina et al. [9] reported the use of methyl-, vinyl- and phenyl polysilsesquioxanes as flame retardants for PP. They showed a decrease in the peak of heat release rate (pHRR) with relatively low concentration (10–20 wt%) of the POSS compounds. Duquesne et al. [12] studied the influence of talc on intumescent PP formulations and showed that composites containing talc were more thermally stable compared to neat polymer. Montezin et al. [19] reported the use of talc and halogenated flame retardants in a PP/PE blend. They showed that the partial replacement of the halogenated flame retardant by talc leads to the same behavior in flame retardancy, reaching V-0 in UL94 test, compared to halogenated alone.

It should be noted that homogeneous dispersion of fillers in polymer matrix and good interfacial adhesion are crucial for the performances of composites. To achieve this goal, several approaches have been considered such as the chemical functionalization of fillers or the use of compatibilizers. In particular, some studies have already reported the modification of layered silicates

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by POSS compounds in order to improve the properties of composites. Zhao et al. [20] showed that montmorillonite (MMT) modified with aminopropylisooctyl POSS improved the mechanical behavior of polyamide 12 (PA12). Ye et al. [21] also studied the influence of a surface treated MMT with the same POSS on the thermal behavior of polystyrene (PS). The authors showed an increase in onset temperature under nitrogen with functionalized MMT compared to pure polymer or composites filled with untreated MMT.

In the present study, surface modification of kaolinite with trisilanolisooctyl POSS was evaluated in terms of fire reaction of PP composites. Kaolinite performance was also compared to talc in PP. Finally, rheological measurements were carried out to assess the relation between viscosity and flame retardancy of composites.

2. Materials and methods

2.1. Materials

Trisilanolisooctyl POSS was used as purchased from Hybrid Plastics (Fig. 1). PP was a homopolymer supplied by Sabic (SABIC® PP 505P, MFR 2.0 g/10 min at 230 °C/2.16 kg).

Two ultrafine layered silicates with close particle size and morphology were used in this study: kaolinite (Kaol) kindly supplied by Vale (Ipixuna-Brazil) and talc (TA) kindly supplied by Imerys (Luznac-France). Commercial designation and characteristics of both fillers are shown in Table 1. Specific surface area was determined by B.E.T. (Brunauer–Emmett–Teller (B.E.T) method, using N₂ as adsorbed gas at 77 K on a Beckman Coulter SA3100 instrument and average particle size (d₅₀) by laser particle-size analysis (Coulter LS230).

2.2. Surface modification of kaolinite

Surface treatment of kaolinite particles was carried out in ethanol/water mixture (96/4). 10 g of kaolinite, 0.3 g of trisilanolisooctyl POSS and 90 mL of an ethanol/water solution were introduced in a 250 ml flask fitted with a condenser. The mixture was then stirred and heated at solvent reflux for 4 h. The mixture was then centrifuged to remove the liquid phase and washed three times with ethanol. The POSS modified kaolinite was dried at 50 °C for 12 h. Surface treated kaolinite is referred as Kaol-POSS.

2.3. Preparation of PP composites

Compositions were extruded using a Clextral BC21 twin-screw extruder (CLEXTRAL SAS & AFREM, Firminy, France). The rotation speed was kept at 150 rpm, temperature ranged between 160 and 200 °C and polymer output was 4.5 kg/h. Square sheets specimens were prepared with dimensions of 100 × 100 × 4 mm³ by injection molding using a 50 ton Krauss-Maffei equipment (Munich, Germany) and temperature range from 180 to 200 °C. The formulations

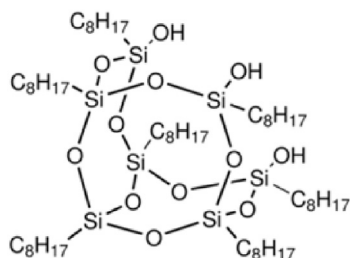


Fig. 1. Trisilanolisooctyl POSS structure.

are showed in Table 2.

2.4. Characterization

Thermogravimetric analyses (TGA) were carried out on 10 ± 2 mg samples at 10 °C/min from 20 to 800 °C under nitrogen flow using a Perkin-Elmer Pyris-1 TGA. A Scanning Transmission Electron Microscopy (FEI Quanta 200 SEM) was used to study the morphology of the samples. All images were obtained under high vacuum at a voltage of 12.5 kV. The cone calorimeter experiments were carried out using a Fire Testing Technology apparatus with an irradiance of 50 kW/m² according to ISO 5660 standard. For each composite three samples were tested and mean values were reported. Viscosity measurements were carried out in dynamic mode at 200 °C using 0.5% strain and a frequency ranging from 10⁻¹ to 10² s⁻¹ (ARES, Rheometric Scientific) using parallel plates geometry. Shear storage modulus (G') and damping factor (tan δ) were evaluated.

3. Results and discussion

3.1. Surface modification of kaolinite

The effect of surface treatment was evaluated by FTIR analysis and showed in Fig. 2. Kristo et al. [22] have reported that kaolinite has five infrared active modes in the 3800–3400 cm⁻¹ region, centered at 3693 (ν₁), 3681 (ν₄), 3667 (ν₂), 3651 (ν₃), ascribed to the “outer hydroxyls” and 3619 (ν₅) cm⁻¹ (“inner hydroxyl groups”). It should be noted that active mode at 3681 cm⁻¹ is only observed using Raman spectroscopy. The kaolinite used in the present work displays bands at 3692, 3665, 3650, and 3617 cm⁻¹, in agreement with the literature. The Kaol-POSS sample shows a band centered at 2900 cm⁻¹ characteristic of C–H bonds and indicates that the POSS was successfully grafted on the kaolinite surface (Fig. 2).

Thermal stability of POSS, Kaol and Kaol/POSS observed by TGA are shown in Fig. 3. The first stage of mass loss observed for the POSS (at approximately 140 °C) may be related to the degradation of silanol groups, while the second mass loss which starts at about 320 °C occurs due to the degradation of isooctyl branches and Si–O cage [23]. Kaol shows a single degradation steep in mass loss between 400 and 550 °C corresponding to the release of structural water (about 14%). Kaol-POSS shows a decrease in the thermal stability in comparison to Kaol. The mass loss starts at about 320 °C which corresponds to the degradation of the Si–O cage from the grafted POSS. The mass loss for Kaol-POSS is about 16.7%, corresponding to a grafting rate of about 5% wt., considering the mass loss of POSS and kaolinite.

3.2. Thermal stability of PP composites

TGA measurements are shown in Fig. 4 and complete results in Table 3. Thermal degradation of PP under nitrogen was well studied and consists in a single mass loss step which starts at about 310 °C [24–27]. PP thermally degrades to volatile products through a radical chain process originated by carbon–carbon bond scission. The addition of Kaol or Kaol-POSS leads to a significant improvement of the thermal stability of PP composites: the initial pure PP decomposition temperature corresponding to a mass loss of 2% wt. is about 347 °C whereas this temperature is shifted to 389 °C for PP filled with talc (PP/TA), 400 °C for PP/Kaol and 400–420 °C for PP/Kaol-POSS as a function of filler loading.

As reported in Table 3 the peak of mass loss rate is 438 °C for pure PP. This temperature is shifted to about 460 °C for all PP/Kaol composites (10, 20 and 30 wt%). For PP/Kaol-POSS an increase was

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