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Thermal and combustion behavior of polyethersulfone-boehmite nanocomposites

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ABSTRACT

In this paper, we report a thorough study on the thermal stability and fire behavior of polyethersulfone (PES) filled with 2 wt% nano-sized aluminum oxide hydroxide particles (boehmite). The nanocomposite was prepared through melt compounding technique in a co-rotating twin screw extruder. The obtained morphology of the composite was studied by scanning electron microscopy (SEM) coupled with elemental analysis, proving that an even distribution of sub-micron boehmite particles was obtained. PES shear modulus, measured by DMA, is increased by 30% in the boehmite nanocomposite. Thermal stability of the produced materials was studied through thermal gravimetric analysis (TGA), whereas the combustion behavior through cone calorimeter and vertical burning (UL-94) tests. Cone calorimeter results show that a significant overall flame retardant effect was observed due to the presence of boehmite nanoparticles, which could not be detected by UL-94 fire scenario where neat PES is already top ranked V0.

1. Introduction

The combustion behavior of polymers and composites is of great importance, especially in those applications where fire risk is not negligible. In particular, since the design and the production of polymer-based items and structural components have exponentially increased, the issue of the reaction to fire has become a key factor for the pursuit of safety. For this reason, there are a large number of published studies regarding the fire performance of most polymers, especially those materials whose fire behavior is problematic [1–3]. In particular, in recent years a big effort was spent to the development of halogen-free flame retardants for polymers, in order to avoid the use of traditional chlorinated or brominated compounds. In this field, much attention was given to the use of nanofillers such as, for instance, layered and needle-like silicates [4–6], polyhedral oligomeric silsesquioxanes (POSS) [7,8] or other inorganic nanoparticles [9,10]. Furthermore, since the requirements related to safety are becoming progressively more stringent, the need to investigate the reaction to fire is involving even polymer whose fire performance is so far considered adequate.

Polyethersulfone (PES) is an amorphous engineering polymer. It has a T_g of 225 °C, good mechanical properties, thermal stability and reaction to fire performance [11]. Despite the increasing importance of PES, according to our literature review, there is a lack in the understanding of the thermal and combustion mechanism of this polymer. Wang et al. [12] prepared $BaTiO_3$/PES nanocomposites using the ultrasonic dispersion and hot-pressing method. They studied the dielectric and thermal properties, demonstrating that $BaTiO_3$/PES composites possessed desirable properties, such as high dielectric constant, low loss tangent, high thermal stability, as well as good processability. For this reason, they suggested $BaTiO_3$-PES composite as a candidate for embedded capacitors under a high temperature environment. Ramanujam et al. [13] reported a study on polyethersulfone-expanded graphite nanocomposites. They observed that ultrasonication of expanded graphite in dichloromethane allows the exfoliation in nanosheets. The effective dielectric constant at low frequency increases with filler concentration. DSC shows an increment of the T_g of PES with 3 wt% expanded graphite suggesting interaction between the polymer and filler.

In this paper, we study the effect of nano-sized boehmite particles in the thermal and combustion behavior of PES. Aluminum oxide hydroxide (γ-AlO(OH)), commonly referred to as boehmite, is a mineral of partially dehydrated aluminum hydroxide with high thermal stability [14–20]. It can be either micro-sized or nano-sized and can have different morphologies, namely spherical, cubic and needle-like shape. It was chosen because it is known to be stable at the common working temperatures of most engineering polymers, such as polyethersulfone.

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2. Material and methods

A low viscosity injection molding grade of polyethersulfone was used as a polymeric matrix. It was kindly supplied by BASF and commercialized under the trade name of Ultrason E1010. It has a melt volume ratio of 150 cm^3/10 min (360 °C–10 kg), a density of 1370 kg/m^3 and a viscosity number (in 0.01 g/ml Phenol/1,2, ortho-Dichlorbenzene, 1:1) of 48 cm^3/g. Boehmite Disperal HP40 (Sasol – Germany), thereinafter in the text referred to as DHP40, was chosen as a filler. It has a nano-sized spherical shape (40 nm) and is based on an aluminum oxide hydroxide mineral.

The nanocomposite was produced by melt compounding in a co-rotating twin extruder (Leistriz 27). The polymer was introduced through the main feeder, while the filler was introduced through the side feeder, in the percentage of 2 wt%. Both PES and boehmite were dried before compounding: PES was dried 4 h at 140 °C (relative humidity 0.02%) and boehmite 3 h at 100 °C. All the processing temperatures were set at 350 °C. In Fig. 1 the screw profile is reported. The samples for the characterizations were produced with a Arburg 50 injection molding machine.

Scanning electron microscopy (SEM) equipped with elemental analysis (Energy Dispersion X-Ray Spectroscopy – EDXS) was used as a technique for investigating the dispersion level of the nanoparticles in the matrix. It was performed with a SEM Leo 1450 VP. A brittle fracture surface was produced introducing the sample in liquid nitrogen, then the samples were sputter coated with gold before the analysis. A field emission scanning electron microscope (FESEM) Zeiss Supra 25 was used to perform a morphological study of the used boehmite.

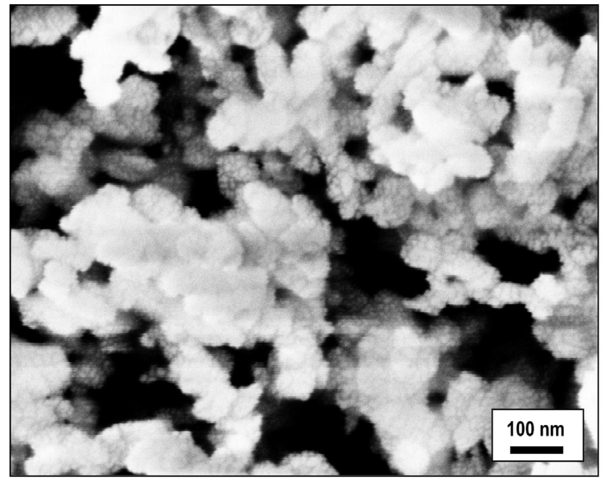
Differential scanning calorimetry (DSC) tests were performed with a TA Instruments equipment, model Q200. A cycle of three dynamic scans (heating – cooling – heating) was performed for each sample, in the range 30–350 °C. All the tests were performed at 10 °C/min.

Dynamic mechanical analysis was performed with a rotational rheometer Rheometric Scientific ARES, model 2KFRT. Temperature ramp tests were performed from 30 to 235 °C at 5 °C/min. The strain was set at 0.005% and the frequency at 1 Hz. The studied parameters were G' and tan δ.

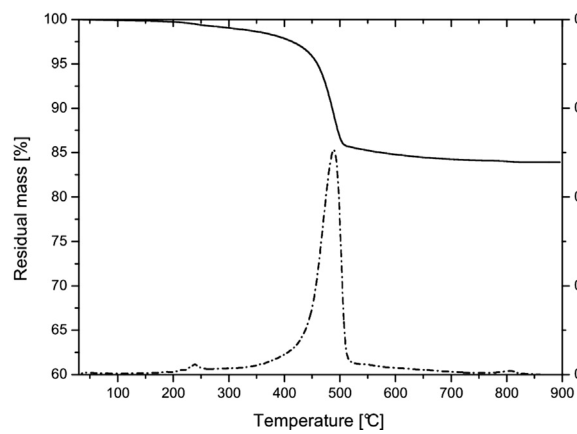
Thermal gravimetric analysis (TGA) was performed with a TA Instruments equipment, model Q500. All the tests were performed in the 30–900 °C temperature range, with a scan rate of 10 °C/min, both in nitrogen and air.

Oxygen consumption calorimeter (cone calorimeter) tests were carried out to evaluate the fire behavior of the produced materials. The tests were performed with a Fire Testing Technology equipment, at a heat flow of 50 kW/m^2, according to standard ISO 5660. The reported results are the average of at least 4 square-shaped samples of 100 × 100 × 3 mm dimension.

UL-94 vertical burning tests were performed in an enclosed laboratory hood, free of induced or forced draft during test, according to ASTM D3801. The dimensions of the tested samples were 125 × 13 × 3.2 mm. Five specimens for every material were tested,



(a)



(b)

Fig. 2. Boehmite Disperal HP40: (a) SEM image and (b) TGA profile (nitrogen).

as recommended by the standard. The test consists in applying the flame for 10 s twice, and measuring the burning time. The other parameters which are recorded for every test are: the mass of the sample before and after the test, whether the flame reaches the top of the sample and whether the cotton is ignited by burning particle drops. Based on the aforementioned data, a material can be classified as VO, V1, V2 and NC where V0 is related to the best performance and NC – non classified – to the worst (i.e. highest burning time, cotton ignited, flame up to the top).

3. Results and discussion

3.1. Boehmite characterization

As a first step of this study, a characterization of the used boehmite was performed. In Fig. 2a a SEM image is shown and it

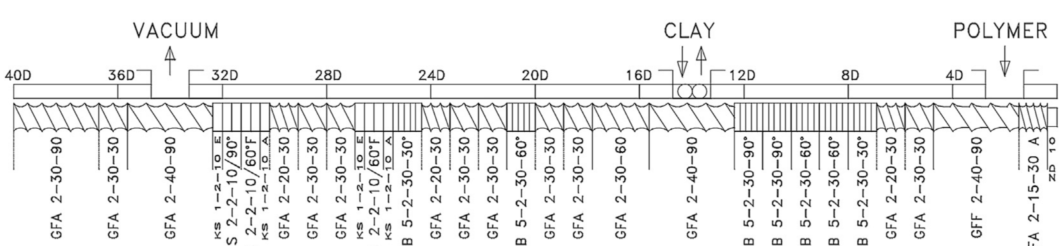


Fig. 1. Used screw profile.