THERMAL AND FIRE BEHAVIOR OF POLYETHERSULFONE/HALLOYSITE NANOTUBE NANOCOMPOSITES

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Abstract
In this work, polyethersulfone (PES)/halloysite nanotube (HNTs) nanocomposites are prepared via a water-assisted extrusion process using –Cl or –OH groups at PES chain ends. The influence of PES chain ends and/or water injection on halloysite dispersion is investigated by scanning electron microscopy. A better dispersion of nanoclay inside the polymeric material is observed for PES with –OH chain ends (PES-OH), while water seems to have almost no effect of the filler dispersion. Based on first morphological results, only PES-OH/HNTs nanocomposites are kept for further investigations. Thermal stability of neat polymer and nanocomposites is studied under both air and nitrogen atmospheres. The presence of halloysite increases the initial thermal degradation temperature of PES due to an improved barrier to mass transfer. The flammability is also investigated combining UL-94 and cone calorimeter tests. The lowest flammability is achieved at the highest HNTs loading.

1 Introduction

Polymer-clay nanocomposites have drawn a great deal of attention in recent years due to the broad range of properties that are improved at low filler contents compared to raw materials. Typically, nanocomposites exhibit improved stiffness and impact resistance, higher thermal and barrier properties as well as reduced flammability [1,2]. These new materials find application in the automotive, electronics, building and furnishing industries.

Polyethersulfone (PES) is a transparent amorphous thermoplastic resin with better high-temperature properties than other conventional engineering plastics, such as good dimensional stability, high glass transition temperature (T_g), very high oxidative and thermal stability as well as very low flammability with a limiting oxygen index around 38 vol% [3,4]. This polymer exhibits also excellent mechanical properties with high modulus, tensile yield strength and impact strength. PES is mainly used for the production of filtration membranes, medical devices, aircraft and automobile parts as well as in the development of new composite materials [5,6].

Recently, halloysite has been reported as new potential clay nanofiller to reinforce polymers [7,8]. Halloysite is chemically similar to kaolinite and exhibits a predominantly hollow tubular structure with mainly SiO groups located at the external surface [9]. Compared to

montmorillonite, there are only weak secondary interactions between adjacent tubes via hydrogen bonds and van der Waals forces. Therefore, no organomodification is required to achieve a homogeneous dispersion of halloysite inside the polymer matrix [10]. Several research groups reported enhanced thermal stability and flame retardancy of polymeric materials in presence of halloysite [11,12]. Such observations are explained by the formation during the combustion process of an inorganic protective layer at the surface of the condensed phase acting as a barrier to heat and mass transport [13].

Among the principal methods for producing polymer nanocomposites, solution mixing process is usually preferred for PES owing to the high T_g of the amorphous polymer [14]. However, this technique is difficult to apply at the industrial scale due to the environmental issues associated with the use of large amount of solvents. Therefore, it is essential to be able to prepare such composites by extrusion, as melt-blending is cost-effective and environment-friendly. However, to the best of our knowledge, no work has already been reported on the elaboration of PES nanocomposites by melt-compounding.

The main goal of this study is to prepare PES/HNTs nanocomposites by melt-blending using two different methods: (i) a conventional extrusion and (ii) a water-assisted extrusion process. This latter technique, fully described in a previous work [15], has been already used to successfully prepare polymer-clay nanocomposites [15,16]. The influence of –OH or –Cl groups at the polymer chain ends on the halloysite dispersion is presented. In a second step, the effect of halloysite nanotubes on the thermal stability and flammability of PES is investigated.

2 Materials and testing methods

2.1 Materials
Commercially available Cl and OH-terminated PES resins were purchased from Solvay. Halloysite nanotubes were provided by Sigma-Aldrich without any chemical modification. Typical specific surface area of this clay is 64 m^2/g; cation exchange capacity of 8 meq/g; pore volume of 1.25 ml/g; and specific gravity of 2.53 g/cm^3.

2.2 Sample preparation
All neat polymers and composites were prepared in a co-rotating twin-screw extruder Krupp WP ZSK25 at 350 °C with a screw speed of 200 rpm. Water (W), when used, was pumped into the extruder at a 50 ml/min flow rate in the high compression zone. Water was then degassed at the end of the extruder using a vacuum pump and hot extrudates were immediately quenched at room temperature and pelletized. Two kinds of composites were elaborated. Halloysite was first melt mixed with PES-Cl with and without water injection at 6wt% HNTs (Table 1). In a second step, PES-OH/HNTs nanocomposites were prepared at two different HNTs loadings (6 and 16 wt%) with and without water injection (Table 1). Specimens for fire tests were produced by compression molding at 350°C for 3 min. Prior to being processed by extrusion or compression molding, PES and composite pellets were dried in a vacuum oven at 120 °C for 48 h.

2.3 Scanning electron microscopy (SEM)
The cryofractured surfaces of PES/HNTs nanocomposites were analyzed using a LEO 932 (Zeiss) scanning electron microscope.

Samples	HNTs [wt%]	W [ml/min]
PES-Cl	0	0
PES-Cl/HNTs6	6	0
PES-Cl/HNTs6-W	6	50
PES-OH	0	0
PES-OH/HNTs6	6	0
PES-OH/HNTs6-W	6	50
PES-OH/HNTs16-W	16	50

Table 1. Composition of PES/HNTs nanocomposites (Polyethersulfone (PES), halloysite (HNTs), water injection rate (W)).

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on a TGA/SDTA 851e (Mettler-Toledo) thermogravimetric analyzer under nitrogen and air atmospheres with a gas flow rate of 100 ml/min. Samples with a mass of 12 ± 0.5 mg were placed in open alumina pans and heated from room temperature to 1000 °C at a constant heating rate of 10 °C/min.

2.5 Fire properties
2.5.1 UL-94 test

The UL-94 vertical test was carried out on samples with dimensions of 127 mm x 12.7 mm x 3 mm according to ASTM D635-77. Five specimens were tested for each composition.

2.5.2 Cone calorimetry

Combustion experiments were carried out using a FFT (Fire Testing Technology) Mass Loss Calorimeter following the procedure defined by ASTM E 906. The specimens with dimensions of 100 mm x 100 mm x 3 mm were irradiated in a horizontal position by applying an external heat flux of 50 kW/m^2. The cone data reported in this work are based on the average of three replicated experiments and are reproducible with variation less than 10%.

3 Results and discussion

3.1 Morphology of PES/HNTs nanocomposites

SEM micrographs show in Fig. 1 the morphology of the different PES/HNTs systems with 6 wt% HNTs. A poor HNTs dispersion is observed for PES-Cl/HNTs nanocomposites prepared with (Fig. 1b) or without (Fig. 1a) water injection. Indeed, most of the tubes are under big aggregates underlined by red circles. Better clay dispersion is achieved using –OH groups at chain ends instead of –Cl groups (Fig. 1c). Most of the tubes are well-dispersed in PES-OH matrix and only few smaller aggregates are still present. Once again, water seems to play almost no role on the filler dispersion during the extrusion process (Fig. 1d). At higher HNTs loading (16 wt%), more aggregates are observed in PES-OH on the whole investigated area, whatever the extrusion process used (Fig. 2a).

By looking at higher magnification (Fig. 2b), it can be seen that some nanotubes are coming out of the matrix (blue circles). Moreover, some cavities are also observed. This result indicates that HNTs do not break in half when the fracture takes place but are preferentially pulled out of the matrix, suggesting a limited interfacial adhesion between filler and polymer.

The good dispersion of halloysite only observed in PES matrix with –OH groups at chain ends could be explained by the better affinity between polymer and filler with the formation of hydrogen bonds between the –OH groups of the polymer chains and the siloxane groups at
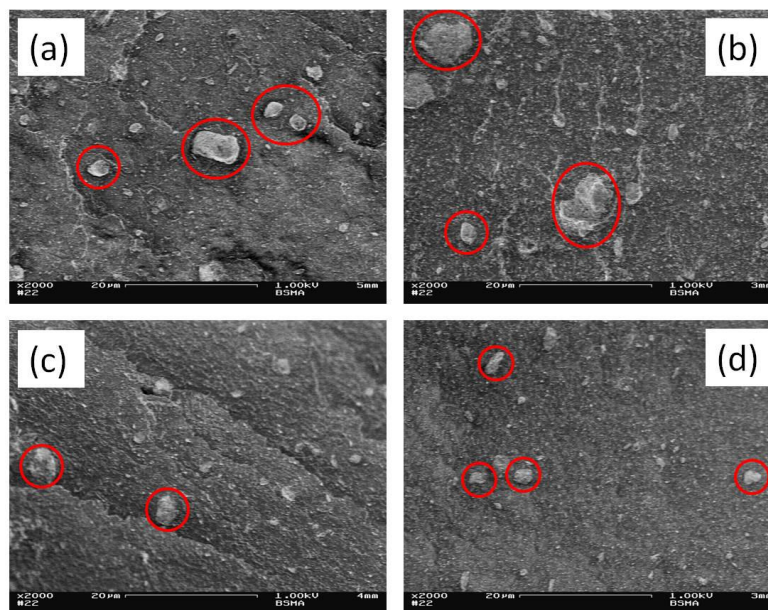
Figure 1. SEM micrographs of: (a) PES-Cl/HNTs6, (b) PES-Cl/HNTs6-W, (c) PES-OH/HNTs6 and (d) PES-OH/HNTs6-W nanocomposites. Red circles underline HNTs aggregates.

the external surface of the tubes. FTIR analyses should be done in the near feature in order to confirm the presence of H-bonds between halloysite and PES-OH.

Finally, as the clay dispersion is quite similar in PES-OH prepared with or without water injection, we decided to keep the more complex system (PES-OH/HNTs-W) to study more in detail the properties as a function of the filler content.
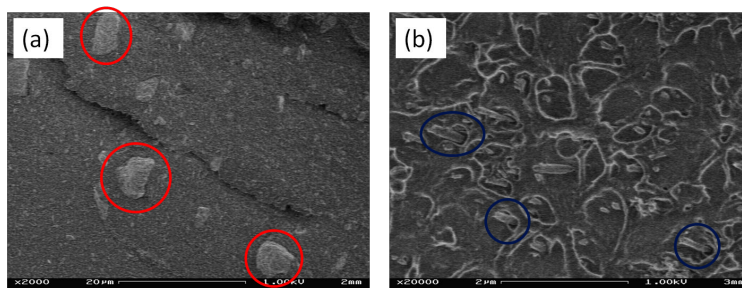

Figure 2. SEM micrographs of: (a) PES-OH/HNTs16-W and (b) PES-OH/HNTs6-W nanocomposites. Red and blue circles underline HNTs aggregates and poor filler/matrix interface, respectively.

3.2 Thermal stability

The thermal behavior of pure PES-OH and composites has been investigated in both inert (N_2) and oxidizing (air) atmospheres. TG and DTG curves are reported in Fig. 3 and 4 for N_2 and air, respectively. Table 2 lists the onset decomposition temperature at 5% weight loss (T_5), the temperature at the maximum weight loss rate (T_{max}), as well as the char yield at 800 °C. Under both atmospheres, the virgin polymer is highly stable with almost no weight loss below 450 °C. The onset decomposition temperature of PES-OH is quite similar in air (483 °C) and in N_2 (475 °C). Therefore, it seems that there is almost no influence of oxygen on the initial degradation process of PES, which suggests that the onset of bond scission is mainly thermal in nature.
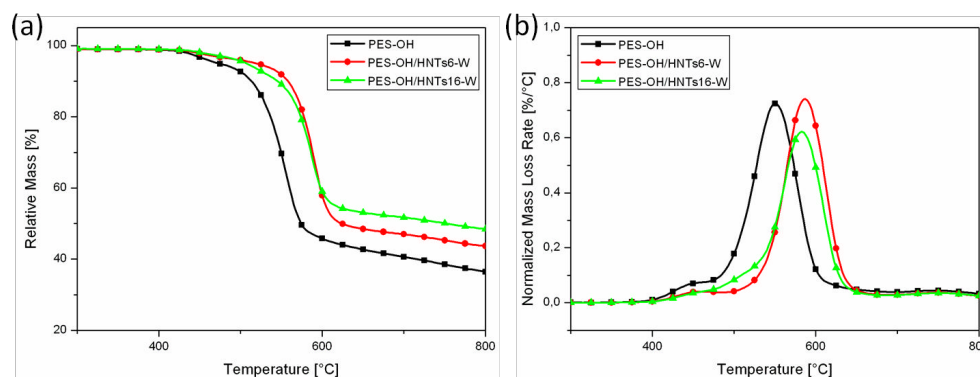
Figure 3. (a) TG and (b) DTG curves under nitrogen of PES-OH and HNTs composites prepared using water-assisted extrusion.

Under nitrogen, PES-OH degrades principally through a one-step reaction (Fig. 3b) resulting in the formation of a highly stable char (36 wt%). Under air, the little shoulder and the two major peaks observed on the DTG curve of PES-OH (Fig. 4b) indicate that the polymer decomposes through a multi-step process completed around 650 °C. The former peak can be ascribed to several degradation reactions including sulfur dioxide exclusion, hydrogen abstraction, dehydration and crosslinking between aromatic carbons [3,17]. The latter peak corresponds to the thermo-oxidative degradation of the char, mainly composed of the aromatic carbon and stable under N_2. Consequently, the char yield at 800 °C is higher in nitrogen than air because of the additional thermo-oxidative degradation of the char in air.

Under both atmospheres, the presence of halloysite in the polymeric matrix increases the onset degradation temperature (Fig. 3a and 4a). For instance, compared to neat polymer, T_5 of PES-OH/HNTs6-W nanocomposite increases by 43 and 19 °C in N_2 and air, respectively. However, at higher HNTs loading (16 wt%), the thermal stability is not further improved. This result can be explained by the presence of more aggregates at higher filler loading as reported by SEM observations (Fig. 2a). The enhanced thermal stability of PES-OH nanocomposites, compared to reference, is mainly due to the formation of a tortuous diffusion path for the oxygen transfer into the polymer and the release of volatile decomposition products. The residue at the end of the thermo-oxidative degradation corresponds to the initial inorganic content of the material (Table 2). Under nitrogen, the additional weight of the char residue at 800 °C, compared to the pure polymer, corresponds also to the halloysite content of the composite.
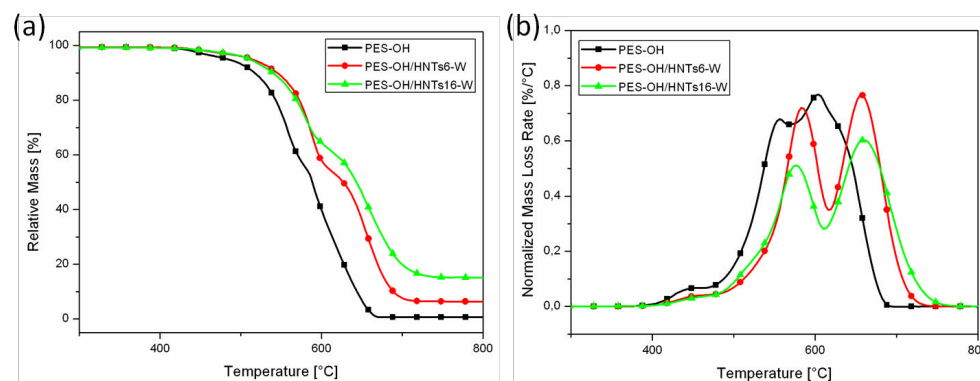

Figure 4. (a) TG and (b) DTG curves under air of PES-OH and HNTs composites prepared using water-assisted extrusion.

Samples	Atmosphere	$T_5/T_{max1}/T_{max2}$ [°C]	Char at 800 °C [wt%]
PES-OH	N_2	475/550/-	36
	Air	483/556/604	0
PES-OH/HNTs6-W	N_2	518/588/-	44
	Air	502/583/658	6
PES-OH/HNTs16-W	N_2	507/587/-	49
	Air	511/578/661	15

Table 2. TGA data of PES-OH and PES-OH/HNTs-W nanocomposites in air and N_2 at a heating rate of 10 °C/min.

3.3 Fire properties
3.3.1 Cone calorimeter

Cone calorimetry is often used as a bench-scale method to evaluate the fire safety properties of polymeric materials. Heat release rate (HRR), especially peak HRR (pHRR), is considered as the most important parameter to describe the fire behavior of a material. This technique has been used in this work to identify the role of halloysite on the flammability of PES.

HRR curves for reference and nanocomposites are presented in Fig. 5a. The most important fire parameters, such as the time to ignition (TTI), pHRR, the total heat released (THR) and the char residue were measured and are summarized in Table 3. The TTI of PES-OH/HNTs-W nanocomposites significantly increases compared to neat polymer and corroborates well with the higher thermal stability reported for PES-OH in presence of clay. Indeed, well-dispersed HNTs hinder the out-diffusion of the volatile decomposition products and delay the flame ignition. This result confirms that the onset decomposition temperature controls the ignition of the burning process.
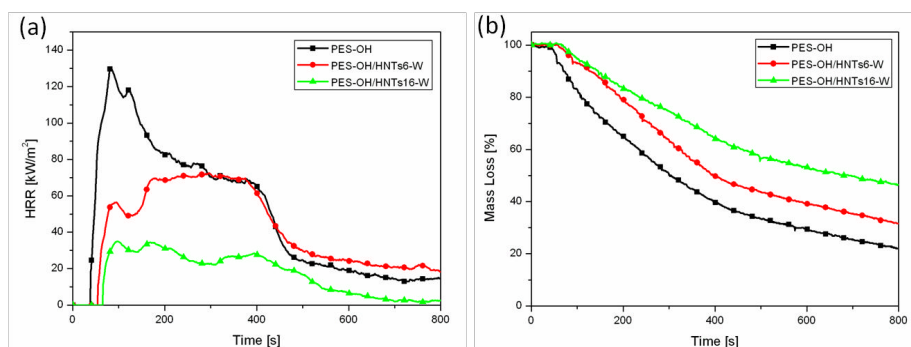

Figure 5. (a) Heat release rate (HRR) and (b) mass loss as a function of time for PES-OH and HNTs composites prepared using water-assisted extrusion (heat flux = 50kW/m^2).

All systems show HRR curves characteristic of char-forming materials. After ignition, a first increase in HRR is observed up to a peak corresponding to the development of a protective char structure that shields the underlying polymer against external heat exposure. Both PES and PES/HNTs nanocomposites produce char under flame and the high thermally stable polymer seems to be the predominant source of carbonaceous residue. In presence of HNTs, pHRR and THR are reduced with increasing the filler content. For instance, the addition of 16 wt% HNTs to PES-OH leads to a 73% reduction in pHRR and a 68% reduction in THR. The burning time is also slightly prolonged for this system (550 s) compared to neat polymer (450 s). The suggested mechanism of action of halloysite nanotubes has already been described in a previous study as an ablative reassembling of the silicate nanotubes at the surface of the condensed phase, resulting in the formation of an inorganic char layer acting as a physical

barrier to both heat and mass transport. In this study, halloysite also acts as an aluminosilicate "skeleton frame" that supports the carbonaceous char formed during the combustion of the polymer. Therefore, the char is tougher and more mechanically resistant than that formed during the combustion of the pure polymer.

Samples	TTI [s]	pHRR [kW/m^2]	THR [MJ/m^2]	Char [wt%]	UL-94
PES-OH	39	130	40	22	V0
PES-OH/HNTs6-W	56	72	33	32	V0
PES-OH/HNTs16-W	65	35	13	47	V0

Table 3. Cone calorimeter data of PES-OH and composites. Tests were conducted at a heat flux of 50kW/m^2.

Fig. 5b shows the mass loss as a function of combustion time for all samples. The total mass loss decreases with increasing the HNTs loading. This result cannot be fully explained by the partial replacement of organic material by inorganic filler. Indeed, the residual mass of PES-OH/HNTs16-W nanocomposite is 25wt% higher than that of pure polymer. Therefore, it seems that fewer gases are evolved during the combustion process of nanocomposites. Once again, this observation confirms that well-dispersed HNTs in PES-OH enable the formation of a mechanically reinforced and more compact carbonaceous-silicate residue that can reduce the number of cracks formed during combustion and, consequently, the fuel feeding the flame.

After extinction of the flame, a phenomenon of afterglow is observed and is directly related to an oxidation process of the carbon-rich char residue. As shown in Fig. 5b, the slow combustion of carbon residues is accompanied by a mass loss, smaller than that observed during the first combustion step.

3.3.2 UL-94
The data from standard UL-94 vertical burning test of the PES-OH/HNTs nanocomposites are reported in Table 3 and show that neat polymer and all nanocomposites achieve a V-0 rating at 3 mm. The pure polymer stops to burn instantaneously after the first application of the flame and self-extinguishes in 1.5 s after the second ignition. PES-OH/HNTs-W nanocomposites with 6 and 16wt% HNTs self-extinguish immediately after both flame applications. These results indicate that such materials are completely stable against this type of ignition. From optical images of the samples (Fig. 6), it can be easily observed that upon ignition, char forming reactions quickly occur in neat PES-OH and enable the formation of a protective layer against the flame.
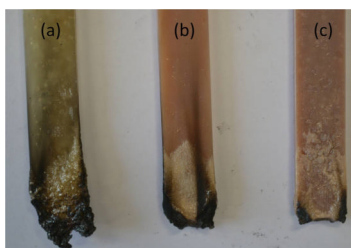

Figure 6. Optical images of: (a) neat PES-OH, (b) PES-OH/HNTs6-W and (c) PES-OH/HNTs16-W after the UL-94 (3 mm) vertical burning test.

The reduced combustion time of PES-OH/HNTs nanocomposites can be related their higher thermal stability compared to the neat polymer. Tests will be reproduced in a near future at a lower thickness (0.8 mm) in order to obtain a better discrimination between the different samples and to confirm this hypothesis.

4 Conclusions

In this work, PES/HNTs nanocomposites have been successfully prepared by melt-blending using a novel "one-step" water-assisted extrusion process. A better HNTs dispersion is observed in PES with –OH chain ends than –Cl. This result can be explained by the formation of hydrogen bonds between the –OH groups of the polymer chains and the siloxane groups at the external surface of the tubes. Moreover, scanning electron microscopy reveals that the use of water injection during extrusion seems to have almost no effect on the clay dispersion. Based on these results, the thermal stability and flame retardancy of PES-OH/HNTs nanocomposites have been investigated. PES-OH exhibits very high thermal stability with almost no weight loss below 450 °C, whatever the atmosphere used. The same initial decomposition temperature in air than N_2 indicates that the onset of bond scission is mainly thermal in nature, without almost any influence of oxygen. Moreover, the use of halloysite in PES matrix enhances the thermal stability of the polymer via the formation of a tortuous diffusion path that delays the release of volatile decomposition products. Adding HNTs reduces the flammability of PES-OH in cone calorimeter experiments, with a lower total mass loss. Better results in presence of halloysite are explained by the formation of a mechanically reinforced and more compact carbonaceous-silicate residue that can reduce the number of cracks formed during combustion and, consequently, the fuel feeding the flame. After flame-out, afterglow is observed for all samples due to char oxidation reactions. Finally, all samples achieve a V-0 rating (3 mm) at the UL-94 test.

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