



Research paper

Contribution of the organo-montmorillonite/graphene pair to the rheological and mechanical properties of polyethylene matrix based nanocomposites



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ABSTRACT

Since the last decade, graphene nanoplatelets with their exceptional physical properties are used as fillers in thermoplastic blends. In this work, the influence of commercial graphene nanoplatelets on properties of a high density polyethylene, in solid and melt states, was investigated, in comparison with the one of organically modified montmorillonite fillers. The use of a compatibilizer, a maleic anhydride grafted polyethylene, led to a clay based nanocomposite, with some improved mechanical and rheological properties, but with disappointing mechanical properties at break. On the other hand, by reducing the viscosity during mixing, the added compatibilizer slightly lowered the degree of dispersion of high aspect ratio graphene particles, weakening the material. More interestingly, the nanocomposite constituted with both clay nanoplatelets and lamellar graphene particles exhibited better reinforcing characteristics, in melt and solid states. This result can be partially explained by the high viscosity of the clay based nanocomposite which helps in the separation of graphene particles during mixing.

1. Introduction

Applicative and fundamental research in the field of nanocomposites, which offer better end-use properties than those of microcomposites, at equivalent filler volume fraction, has significantly evolved. Since two decades, the relations between processing, structure and macroscopic behavior of this class of nanomaterials were thoroughly studied, as reviewed by Camargo et al. (2009). In particular, organically modified montmorillonite (OMt) is now successfully used as lamellar nanofiller for the elaboration of polar or apolar thermoplastic based nanocomposites (Ray and Okamoto, 2003), presenting improved mechanical (Alexandre and Dubois, 2000; Kato et al., 2003; Hotta and Paul, 2004; Aït Hocine et al., 2008), barrier (Alexandre and Dubois, 2000; Kato et al., 2003; Hotta and Paul, 2004; Alexandre et al., 2009) and flammability resistance (Gilman et al., 2000) properties. Moreover, melt-state rheological properties of OMt based nanocomposites have also attracted significant attention (Krishnamoorti and Yurekli, 2001), because of their relevance in the identification of the processing/structure/rheological properties relations (Médéric et al., 2006). More

recently, graphene (G), which is the fewest layer limit of graphite, has emerged as a bidimensional material, with a high aspect ratio and exceptional properties (Zhu et al., 2010). Various routes leading down to the individual graphene layer, such as mechanical exfoliation (Novoselov et al., 2004), chemical conversion of graphite to graphene oxide (Stankovich et al., 2007), chemical vapor deposition (Kim et al., 2009), and total organic synthesis (Watson et al., 2001), have been largely reviewed by Allen et al. (2009). But some advances are still required (Singh et al., 2011), especially in the low cost production of large amounts of graphene nanoplatelets (Zhu et al., 2010). 2-D graphene is used as filler for polymer based nanocomposites (Kuilla et al., 2010; Dhand et al., 2013), because it presents a great potential for applications requiring improved electrical, thermal, mechanical and barrier properties (Potts et al., 2011).

However, for an apolar polyolefin matrix, such as polyethylene, the incorporation of a compatibilizer, that is commonly a maleic anhydride grafted polyethylene, is required in order to obtain an organically modified montmorillonite based nanocomposite (Hasegawa et al., 1998) or a graphene based nanocomposite (Schniepp et al., 2006; Kim

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et al., 2011; Seo et al., 2013; Vasileiou et al., 2014). In this case, graft ratio and average molar mass of the compatibilizer, as well as compatibilizer/filler ratio, play a key role in the final structure and resulting physical properties of the thermoplastic based nanocomposite. These parameters have thoroughly been studied for clay based nanocomposites (Hotta and Paul, 2004; Chrissopoulou et al., 2005; Wang et al., 2005; Durmus et al., 2007), but are still in discussion for graphene based nanocomposites (Seo et al., 2013; Mittal and Krauss, 2014).

On the other hand, the melt intercalation technique is often used for the elaboration of polyolefin based nanocomposites because it requires no toxic solvent and it is practical for manufacturing in large scale (Zhang et al., 2010).

OMt based nanocomposites are characterized by the existence of a three-dimensional percolated network mesostructure at low clay mass fractions, usually $\sim 2\%$ for polar matrix (Utracki and Lyngaae-Jørgensen, 2002) or polyolefin/compatibilizer matrix (Durmus et al., 2007). The low mass fraction threshold is explained by the fine dispersion of anisometric OMt nanoparticles within thermoplastic matrix. It was put in evidence from linear or nonlinear properties in melt state (Hoffmann et al., 2000; Ren et al., 2000; Utracki and Lyngaae-Jørgensen, 2002; Aubry et al., 2005; Durmus et al., 2007) and in solid state (Ait Hocine et al., 2008; Hassan et al., 2015), and, to a lesser degree, from gas barrier (Alexandre et al., 2009) and thermal (Hassan et al., 2015) properties. Similarly, the incorporation of a low percentage of graphene into a polyolefin matrix was shown to significantly improve mechanical, rheological and thermal properties (Song et al., 2011; El Achaby et al., 2012; El Achaby and Qaiss, 2013), because graphene nanosheets are well-dispersed and exhibit a high specific surface area, especially favoring the efficient transfer of stresses through the matrix/filler interface (Srivastava et al., 2011).

Recent studies have shown that it is conceivable to improve the dispersion of carbon black particles or carbon nanotubes by incorporating them with organically modified montmorillonite nanoplatelets into an elastomer (Pradhan et al., 2015; Annadurai et al., 2016) or a thermoplastic (Ma et al., 2007; Silva et al., 2014) matrix. The apparent synergy between the two fillers leads to an improvement of flame retardancy, mechanical, electrical and acoustic properties. Synergy between fillers in G OMt polylactic acid nanocomposites was also reported (Bouakaz et al., 2015).

The paper focuses on the influence of composition on structural, thermal, mechanical and rheological properties of thermoplastic based nanocomposites constituted of a compatibilizer/polyethylene matrix filled with OMt, G, or OMt and G nanoplatelets, aiming at the study of the mechanisms of a possible synergy between the two kinds of fillers.

2. Experimental part

2.1. Materials

A high density polyethylene, noted PE in the text, referenced as HDPE 5502 and supplied by POLYMED, was used as matrix. Its density is 0.94 g/cm^3 and its melting point is $139.9 \text{ }^\circ\text{C}$. The number average molar mass is $17,300 \text{ g/mol}$, corresponding to a degree of polymerization of about 600, and the polydispersity index is 7.8 (Liu et al., 2010). A maleic anhydride grafted polyethylene, referenced as Orevac® 18,507, supplied by Arkema was used as compatibilizer, noted grPE in the text. The maleic anhydride grafting level is inferior to 1%. The density and the melting point of the compatibilizer are 0.95 g/cm^3 and $128 \text{ }^\circ\text{C}$, respectively. The Newtonian complex viscosity of both thermoplastics, measured at $160 \text{ }^\circ\text{C}$, is: $\eta_0^* \sim 250,000 \text{ Pa}\cdot\text{s}$ and $\eta_0^* \sim 55,000 \text{ Pa}\cdot\text{s}$ for the PE matrix and the compatibilizer, respectively. The compatibilized blend obeys to a blending law, meaning that the two thermoplastics are miscible, hence a Newtonian viscosity of $\sim 170,000 \text{ Pa}\cdot\text{s}$ for the blend constituted of 40% of compatibilizer used in this work.

Clay and graphene particles were added to the matrix. The clay is an

organically modified montmorillonite, namely Cloisite® C20A, commercialized by Southern Clay Products (Gonzales, Texas, TX). This organoclay is a dimethyl dihydrogenated-tallow ammonium exchanged montmorillonite. The individual C20A particles are nanoplatelets with $\sim 1 \text{ nm}$ thickness and $\sim 500 \text{ nm}$ length. The density of C20A organoclay is $\sim 2 \text{ g/cm}^3$. Polar graphene particles, referenced N006-P nano-graphene platelets and supplied by Angstrom Materials (Ohio), present an oxygen percentage of 4%, average x-y dimensions less than $5 \mu\text{m}$ and a thickness ranging from 10 to 20 nm. The density of graphene is also close to 2 g/cm^3 .

2.2. Preparation of nanocomposites

All samples have been prepared by simultaneous melt mixing in a Haake Rheomix 600 internal mixer, at a temperature of $160 \text{ }^\circ\text{C}$. The blade rotational speed was of 100 rpm during 6 min. The processing conditions, hence the resulting specific mixing mechanical energy (Médéric et al., 2009), were chosen to avoid the degradations of the matrix and compatibilizer and, more particularly, that of the organic modifier of clay (Xie et al., 2001). Polymers and fillers were manually pre-mixed before being thrown into the mixer.

The samples were pelletized and processed by compression molding at $160 \text{ }^\circ\text{C}$ between 2 mm thick plates. Pressure was increased by steps from 0 to 25 MPa, in order to avoid the formation of air bubbles.

The compositions of all samples are listed in Table 1, in filler mass fractions ϕ_m .

In the study, the compatibilizer mass fraction was fixed at 40%, which was shown to be a relevant content in order to obtain exfoliated OMt polyolefin/compatibilizer nanocomposites (Lertwimolnun and Vergnes, 2005). Moreover, in the case of G polyolefin/compatibilizer, the (G:compatibilizer) ratio is usually chosen ranging from (1:3) to (1:10) (Seo et al., 2013). At last, for the G OMt PE/grPE nanocomposite, the ratio of (G:OMt) was chosen (1:1), which was shown to be the most interesting in terms of structural and mechanical properties for multi-walled carbon nanotubes/organically modified montmorillonite hybrids (Pradhan et al., 2015).

2.3. Characterizations

2.3.1. Structural characterization

Samples were microtomed under a frozen atmosphere into liquid nitrogen and their nanostructures were observed by transmission electron microscopy (TEM), using a JEOL JEM-1230 microscope at 120 kV.

2.3.2. Differential scanning calorimetry

The influence of graphene or/and clay particles on the PE crystallinity was studied from DSC measurements conducted on a Perkin-Elmer DTA-7, under a nitrogen atmosphere. The samples of about 10 mg were heated from room temperature up to $250 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C/min}$, held at $250 \text{ }^\circ\text{C}$ for 10 min, then were cooled from $250 \text{ }^\circ\text{C}$ to

Table 1
Compositions (wt%) of the studied materials.

| Samples | PE | OMt | G | grPE |
|---------------|-----|-----|----|------|
| PE | 100 | 0 | 0 | 0 |
| grPE | 0 | 0 | 0 | 100 |
| PE/grPE | 60 | 0 | 0 | 40 |
| G PE | 98 | 0 | 2 | 0 |
| | 95 | 0 | 5 | 0 |
| | 89 | 0 | 11 | 0 |
| G PE/grPE | 55 | 0 | 5 | 40 |
| OMt PE | 95 | 5 | 0 | 0 |
| OMt PE/grPE | 55 | 5 | 0 | 40 |
| G OMt PE/grPE | 50 | 5 | 5 | 40 |

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