



Research paper

Combined effect of epoxy functionalized graphene and organomontmorillonites on the morphology, rheological and thermal properties of poly (butylenes adipate-co-terephthalate) with or without a compatibilizer



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ABSTRACT

In this work, clay polymer nanocomposites (CPN) with simultaneous dispersion of graphene and organomontmorillonites (OMt) in a poly (butylene adipate-co-terephthalate) (PBAT) biodegradable matrix were prepared, using the melt-blending technique. Two different OMt were used non polar Cloisite15A and polar Cloisite30B with a composition of 3 mass% as well as epoxy functionalized graphene (EFG) with different compositions (1, 3, 5 mass%). The morphology and thermal properties of OMt/PBAT, EFG/PBAT and OMt-EFG/PBAT nanocomposites were studied. A compatibilizing agent (PBATgMA) was elaborated by grafting maleic anhydride on PBAT chains. The effect of incorporation of this compatibilizer on the different nanofillers dispersion in PBAT matrix was studied. The structure of the nanofillers/PBAT nanocomposites was examined using X-ray diffraction analysis and transmission electron microscopy (TEM). The co-addition of EFG with OMt allowed a better dispersion of these nanofillers and more intercalated structures were obtained. The rheological results showed an increase of the storage modulus G' in the different nanofillers/PBAT nanocomposites, particularly after the co-addition of OMt and EFG. The thermal properties evaluated by TGA were sensibly improved by the association of these nanofillers. From all these results, it can be speculated that a synergism phenomenon between graphene and OMt was produced in the PBAT matrix. However, this phenomenon was reduced after the addition of PBATgMA compatibilizer, probably because of repulsive interactions were produced between this compatibilizing agent and the epoxy functionalized graphene.

1. Introduction

The development of biodegradable polymers has been a subject of great interest in materials science for the protection of the environment. Biodegradable polymers, such as polyglycolide (PGA), polydioxanone (PDS), poly(ϵ -caprolactone) (PCL), poly(hydroxyl-butyrates) (PHB) etc. can be degraded in bioactive environments by organisms, such as bacteria, fungi and algae or by hydrolysis in buffer solutions or seawater. Several applications have been proposed for these polymers in the fields of medicine, agriculture and packaging. In particular, synthetic biodegradable polymers such as polylactide, poly (butylene adipate-co-terephthalate) (PBAT) and poly(2-hydroxyethyl-methacrylate) (PHEMA) have attracted special attention because they enable a better control of their physicochemical properties and also because they have

been successfully used in clinical applications (Ciccione et al., 2001; Mohanty and Nayak, 2009; Fukushima et al., 2012).

Among all of the biodegradable plastics mentioned above, the aliphatic aromatic Poly(butylene adipate-co-terephthalate) (PBAT) has attracted great attention because it has excellent softness and ductility, and its high elongation at break makes it suitable for food packaging and agricultural film applications (Averous and Boquillon, 2004; Wang et al., 2015). It offers properties similar to those of low density polyethylene (LDPE) because of its high molar mass and its branched molecular architecture. It is based on monomers of adipic acid, butanediol and terephthalic acid. The aromatic part in the PBAT reinforces the copolymer structure up to a maximum of 40 mass% of terephthalic acid, without changing the biodegradability of the copolyester chains. The aliphatic part is responsible for its biodegradability. This type of

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polymer can be synthesized by bulk condensation process and is fully biodegradable (Averous and Boquillon, 2004; Mukherjee et al., 2014).

However, PBAT has some drawbacks such as brittleness and thermal degradability at a temperature not far above the melting point. The preparation of blends or composites is the most common route to improve polymeric properties. In particular, CPN, in which the reinforcing component is of nanometric scale, showed great promise in improving those properties (Mohanty and Nayak, 2009). CPN have drawn much attention in the past few decades. It is well recognized that the addition of nanofillers to polymers can result in materials that have significantly improved properties. To this end, carbon nanotubes, montmorillonite, graphene, and graphene oxide were added as high performance reinforcing nanofillers in various polymers (Hu et al., 2013; Gao et al., 2014; You et al., 2014).

Montmorillonite (Mt) is one of the most common layered silicates used in the preparation of CPN (Liu and Wu, 2001; Wan et al., 2005; Carli et al., 2011; Le Moigne et al., 2014; Yahiaoui et al., 2014; Issaadi et al., 2015; Ge et al., 2015). Montmorillonite is a crystalline 2:1 layered clay mineral with a central alumina octahedral layer sandwiched between two silica tetrahedral layers. It has a hydrophilic character because of the presence of inorganic cations (Na^+ , Ca^{2+}) in their basal distance. However, an ion exchange reaction into the clay mineral basal distance with organic cations, such as ammonium alkyl group, is generally needed in order to promote the compatibility between polymers and clay minerals. Several studies on Mt-PBAT nanocomposite were performed and showed the formation of intercalated structures due to the good dispersion of clay in the matrix (Chivrac et al., 2006; Mohanty and Nayak, 2009; Chen et al., 2011). Several authors used organically modified montmorillonites (C20A, C15A, C30B, ...) as nanofillers in the elaboration of CPN because they generally lead to a high level of dispersion (Fukushima et al., 2012; Meng et al., 2012; Gomari et al., 2012). Fukushima et al. (2013) studied Mt-PBAT nanocomposite using modified montmorillonite (C30B and C20A) and unmodified one (Mt). The authors showed that C30B exhibited higher dispersion in PBAT matrix compared to Mt and C20A, due to the higher attractive interactions between the carbonyl groups of PBAT and the hydroxyl groups of C30B layers.

On the other hand, since the discovery of graphene in 2004 by Geim, it is the subject of particular interest in the field of polymer nanocomposites due to its exceptional electrical, thermal and mechanical properties (El Achaby et al., 2012; Bai et al., 2011). However, when graphene is incorporated into a biodegradable polymer matrix, the corresponding properties of the resulting materials are usually rather poor, particularly for quantities lower than 5 mass% of graphene, owing to its aggregation and the weak interfacial interactions between the graphene layers and the polymer chains (Bouakaz et al., 2015). In a study realized by Mittal et al. (2014), the addition of thermally reduced graphene to Poly amide (PA), PLA and PBAT matrices showed that PA nanocomposite exhibited extensive exfoliation with a large number of single graphene platelets, while the others were not fully exfoliated. Feng et al. (2014) obtained a similar result by working on Graphite-PBAT biocomposites. X-ray diffraction showed no change in the graphite reflection after its incorporation in the PBAT matrix and TEM analysis confirmed this result.

To improve the dispersion of organoclays or graphene in a polymer matrix, interfacial adhesion between organomontmorillonite (OMt)/polymer and graphene/polymer should be improved. This can be performed by using compatibilizing agents containing grafted maleic anhydride (Mohanty and Nayak, 2010; Mohanty and Nayak, 2012; Wu, 2012; Issaadi et al., 2015; Chen and Yang, 2015). In graphene oxide (GO) PLA nanocomposites, a better dispersion of GO platelets in PLA matrix was observed using a PLAgMA compatibilizer (Issaadi et al., 2016a) leading to an improvement of its thermal stability and barrier properties.

Epoxy Functionalized Graphene (EFG)-PLA nanocomposites prepared by melt mixing were studied by Bouakaz et al. (2015). The results

showed that EFG was poorly dispersed in the PLA matrix for compositions ranging from 1 to 7 mass %. Issaadi et al. (2016b) reported that the use of maleic anhydride grafted PLA enhanced the dispersion of EFG in PLA matrix leading to the improvement of mechanical and barrier properties.

More recently, combination of Mt, GO and graphite... could be found in literature as a route for CPN production that favors an increase in the dispersion of nanofillers in polymer matrices as discussed in the following. A study on Cloisite 30B-expanded graphite/PLA nanocomposites was performed by Fukushima et al. (2010). A good improvement in all the studied properties was noticed after this co-addition. A similar result was obtained by Silva et al. (2014) after the introduction of the mixture of carbon nanotubes (CNT) with clay minerals (Mt Na +, C30B) in a high density polyethylene (HDPE) matrix. According to their TEM and XRD analysis, this co-addition resulted in a better dispersion of both nanofillers in the HDPE matrix compared to the binary CPN, leading to an improvement in thermal and mechanical properties. Recently, Bouakaz et al. (2015) showed, by rheology and TEM analysis, that the association of clay minerals (C15A, C30B) with epoxy functionalized graphene (EFG) improved the mechanical and barrier properties of PLA due to the good dispersion of both nanofillers in the matrix. However, no study has been performed on PBAT, nor on the effect of MA grafted PBAT compatibilizer on OMT-EFG/PBAT nanocomposites.

In the present work, two effects on the morphology, rheological and thermal properties of poly (butylene adipate-co terephthalate) biodegradable matrix were evaluated. Firstly, the effect of addition of epoxy functionalized graphene (EFG), at various compositions of EFG, with & without PBATgMA compatibilizer is evaluated. Secondly, the effect of the incorporation of OMT-xEFG mixtures containing 3 mass% of Omt and various loading of EFG with & without PBATgMA compatibilizer is studied. The dispersion state of these nanofillers in the matrix and the morphology of the resulting CPN were evaluated by rheological measurements, XRD analysis and TEM microscopy. The thermal stability was measured by thermo-gravimetric analysis (TGA).

2. Experimental part

2.1. Materials

The Poly (butylene adipate-co-terephthalate) (PBAT) with trade name Ecoflex®F Blend C1200 was supplied by BASF. It is biodegradable, statistical, aliphatic-aromatic co-polyester based on the monomers 1,4-butanediol, adipic acid and terephthalic acid in the polymer chain. The basic properties of this co-polyester are: density of 1.25–1.27 g/cm³, glass transition temperature (T_g) of -29°C and melting point (T_m) of 110–120 °C.

The modified Mt (C30B and C15A) were supplied by Southern Clay Products. According to the supplier, natural Mt was modified with methyl tallow bis-2-hydroxyethyl ammonium and dimethylhydrogenated tallow ammonium to synthesize Cloisite® 30B and 15A, respectively. The epoxy functionalized graphene (EFG) was obtained from the company NANOVIAMANUFACTURER (France). The PBATgMA compatibilizer was synthesized by melt blending technique in a twin screw extruder, at a temperature of 140 °C and screw speed of 80 rpm, using 3 mass% of maleic anhydride (MA) and 0.5 mass% of benzoyl peroxide (BPO).

2.2. Preparation of the samples

The PBAT matrix, organomontmorillonites and the epoxy functionalized graphene were dried at 60 °C for 6 h, in an oven. For each sample, a physical mixing was performed prior to melt blending. Subsequently, the mixed ingredients were introduced in a twin-screw extruder (5 & 15 Micro Compounder DSM Xplore Model 2005) and blended at 80 rpm for 6 min at a temperature of 140 °C. Finally, the

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