



Research paper

Lignosulfonate interleaved layered double hydroxide: A novel green organoclay for bio-related polymer

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ABSTRACT

New organic inorganic layered double hydroxide (LDH) organoclays are assembled through coprecipitation with lignosulfonate (LS) interleaved inorganic host structure sheets. The biopolymer is found to accommodate the interlayer space adopting a bilayer molecular arrangement resulting in a basal spacing of 2.54 nm. However the crystallinity of the resulting bio-organoclay is weak, probably due to the difficulty of the inorganic sheets to be built on amorphous polymer chain, the latter inducing low structural ordering. An organoclay of composition Zn_2Al/LS is subsequently used as filler in three bio-related polyesters, poly(lactic acid) (PLA), poly(butylene) succinate (PBS) and poly(butylene adipate-co-terephthalate) (PBAT). Melt polymer extrusion using 5 wt.% organoclay loading yields polyester nanocomposite with a nanocomposite structure largely intercalated for both PLA and PBS (Δd (expansion) > 6 nm) while a non miscible structure is obtained for PBAT. The incorporation of hydrophilic Zn_2Al/LS platelets decreases the water/polymer contact angle of about 10° for the LDH/LS PBAT composite only. A strong increase of the complex viscosity $|\eta^*|$ is observed for both nanocomposites Zn_2Al/LS PLA and PBS compared to the polyester itself. This is explained on the basis of a chain extender behavior of the intercalated Zn_2Al/LS platelets towards polymer chains as evidenced on the Cole Cole representation showing an increase of the real viscosity in the low- ω region. In opposition a strong decrease in $|\eta^*|$ is observed for PBAT, underlining a plasticizing effect of the organoclay filler. Comparatively, the thermal stability of PLA is slightly enhanced with an increase of $T_{0.5}$ value while PBS and PBAT bio-nanocomposites degrade at slightly lower temperature.

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1. Introduction

The ever-growing environmental concern framed into an ever-stronger regulation is currently stimulating intense research all over the world to replace fossil energy-based polymer. Indeed there is a lot at stake facing this environmental concern, and the problem may be partially solved by recycling or using alternative degradable materials. Taking into account the requirement for a sustainable development such alternative should also be of interest in terms of performance. For instance biodegradable polymers are interesting not only in disposable packaging but also for different applications such as bone substitute, scaffold and drug carrier for controlled release.

To overcome such issues, biodegradable nanocomposite are more and more considered as the “next generation” for the future (Domb et al., 1997; Pandey et al., 2005; Tsuji and Horikawa, 2007), this with the possible combination with environmental-friendly organoclay as filler.

Indeed biopolymers or bio-degradable polymers candidate to replace polyolefin suffer generally of poor physical properties and consequently their applications are up to now limited while the incorporation of organoclays may provide mechanical reinforcement, barrier effect as well as fire retardancy properties, thus fulfilling the specific requirements for their potential use.

Organo-modified clays are extensively studied for their possibilities to enhance polymer properties (Paul et al., 2003), and among them layered double hydroxide (LDH) materials present a certain advantage (Leroux, 2006). Indeed different authors have pointed out the versatility of LDH materials for fabricating nanocomposites (Ding et al., 2006; Evans and Duan, 2006), as the lamellar nature of LDHs permits host guest chemistry and intercalation reactions, which invoke considerable attention from material designers (Leroux et al., 2010). Layered Double Hydroxide also called “anionic” clay in comparison to smectite-type materials is formed from edge-sharing octahedral, and its structure is described from the substitution divalent by trivalent cations in the brucite $Mg(OH)_2$. The resulting cation composition $M^{II}_{1-x}M^{III}_x(OH)_2$ with x being the relative substitution rate generally ranging as $0.20 < x < 0.33$, endows a positive charge to the sheet counterbalanced

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by the presence of anion in the interlayer space. The surface covered by hydroxyl groups and the great versatility in the cation and anion exchange with suitable organic molecule are highly suitable in flame retardancy application (Evans and Duan, 2006) and the presence of hydroxyl groups renders the particles hydrophilic. Lateral dimensions through the LDH plate ranging from 100 nm to 1–2 μm , and a width of 1 to 3 nm for the organo-modified hybrid platelets give rise to aspect ratio between limits of 100 to 2000, which are potentially interesting for the increase of tortuosity (permeation) and for the mechanical reinforcement (Utracki et al., 2007).

Poly(esters) are among the most promising materials for the production of high-performance and environmental-friendly biodegradable polymer and among them, polylactic acid (PLA), poly(butylene) succinate (PBS) (Lim et al., 2011a,b), and polybutylene adipate terephthalate (PBAT) (Chen et al., 2011; Mohanty and Nayak, 2010; Raquez et al., 2011; Siegenthales et al., 2012; Yang and Qiu, 2011) and the corresponding mixings PLA/PBAT (Kumar et al., 2010; Li et al., 2011) PBS/PBAT (Ibrahim et al., 2010) have recently received a lot of attention.

PLA and PBS are linear aliphatic hydrophobic thermoplastic polyesters. PLA is produced from agricultural resources and by ring-opening polymerization of lactides, and can be easily degraded through hydrolytic process (Grizzi et al., 1995) or by enzymatic way (Edlund and Albertsson, 2001), and it suffers from heat distortion temperature, brittleness, low elongation and gas barrier properties. PBS is synthesized by polycondensation of 1,4-butanediol with succinic acid and presents some drawbacks such as low hydrolysis resistance, softness, tensile, gas-barrier properties and melt-viscosity not sufficient for processing for a practical end-use application (Zhou et al., 2010). PBAT, a biodegradable aliphatic-aromatic polyester, named as Ecoflex® (Siegenthales et al., 2012) combines biodegradability known from its aliphatic moieties with mechanical properties from its aromatic moieties.

The dispersion of organo-modified LDH into biodegradable polymer was scarcely reported, including poly(caprolactone) (PCL) (Mangiacapra et al., 2007; Sorrentino et al., 2005), but recent gain in interest is reported for PLA (Chiang et al., 2011; Ha and Xanthos, 2010; Katiyar et al., 2011; Mahboobeh et al., 2010; Wang et al., 2010) and specifically for assessment of the suitability of the polymer films for use as food contact materials (Schmidt et al., 2011) as well as drug delivery system such as LDH framework dispersed into PLA to vehicle ibuprofen (Dagnon et al., 2009) or alendronate (Chakraborti et al., 2011). This is also available for PBS with functionalized filler for ecological photoactive surface (Kafunkova et al., 2010). Comparatively some studies concern the dispersion of commercially-available organically modified montmorillonite with a particular interest for poly(butylenes succinate-co-adipate) (Dean et al., 2009; Ray and Bousmina, 2006).

Having in mind that the filler in its entire composition should be “green”, it implies that the organo modifying molecule should be bio-eminent or at least environmentally benign, while LDH platelets (of selected composition) are considered as biocompatible (Bugatti et al., 2011; Choy et al., 2007; Costantino et al., 2008; Oh et al., 2009) and as possible food contact materials (Schmidt et al., 2011). Moreover it is well known that the inorganic LDH host structure presents the ability to accommodate cumbersome macromolecule, such as DNA (Choy et al., 1999), alginate (Leroux et al., 2004) and other polysaccharides (Darder et al., 2005). Lignosulfonate (LS), a water-soluble biopolymer obtained from wood industry is here selected. However the fact that lignosulfonate is known as efficient plasticizers in making concrete (Collins et al., 2012), debundling of single-walled carbon nanotubes (Liu et al., 2007), destructuring of inter- and intramolecular interactions within bionanocomposites (Oliviero et al., 2011) as well as presenting a strong hydrophilic character makes it at the first glance not really promising to organo-modify LDH platelets. In contrast the biodegradability of PBAT bio-nanocomposite showed an increase in the rate of biodegradability using Na-montmorillonite due to its hydrophilic nature (Mohanty and Nayak, 2010). Therefore it is here crucial to know

whether the dispersion of such appealing bio-concerned LDH organoclay is efficient as filler for polymer.

LDH/LS assembly first characterized by a combination of techniques (XRD, FTIR, and solid state ^{13}C CPMAS NMR) is subsequently dispersed through polymer melt extrusion into PLA, PBS and PBAT, respectively. The polymer dispersion is scrutinized by low angle XRD, and the microstructure is evaluated by rheology and addressed as a function of the dispersion of the bio-hybrid LDH filler. A series of biodegradable polymer nanocomposites, hereafter noted as PLA:LDH/LS, PBS:LDH/LS and PBAT:LDH/LS, is successively characterized by X-ray diffraction, and rheology to decipher the attractive or plastizing role of the organoclay. Finally the thermal properties of the bionanocomposite are also studied.

2. Experimental section

2.1. Materials

ZnCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros, 99%), NaOH (Acros, 97%) and water-soluble anionic polyelectrolyte lignosulfonate sodium polymer (Aldrich, $\text{C}_{10}\text{H}_{12}\text{O}_5\text{SNa}$, $M_n = 7000 \text{ g} \cdot \text{mol}^{-1}$, $M_w = 52,000 \text{ g} \cdot \text{mol}^{-1}$, CAS # 8061-51-6) were used as received. Poly(lactic acid) (CAS#33135-50-1) (PLA, $-(\text{CH}(\text{CH}_3)\text{CO}-\text{O})_n-$) density of 1.25 g/cm^3 , glass transition temperature (T_g) of 60.7°C and melting point (T_m) of 165.1°C was supplied by Natureworks (4042-D, USA). PBS (CAS#25777-14-4) EnPol G-4560 (MI = 1.5 g/10 min , $T_m = 115^\circ\text{C}$) was provided by Ire Chemicals Co. Korea. Statistical copolyester PBAT (Ecoflex) was supplied by BASF Company.

2.2. Organo-modification of LDH

The cation LDH composition was Zn_2Al , and the preparation of the hydrothermal-like hybrid materials was performed using the so-called coprecipitation method. Experimentally, solution of lignosulfonate ($2 \cdot 10^{-2} \text{ M}$) was prepared, and 250 ml solution of the salts (Zn; $2 \cdot 10^{-2} \text{ M}$ and Al; $1 \cdot 10^{-2} \text{ M}$) was added dropwise to the previous solution. During the addition, the reaction was kept under nitrogen atmosphere in order to avoid contamination by carbonate and the pH was kept constant at $\text{pH} = 9.5 \pm 0.1$ with the addition of NaOH. The slurry was aged in the mother liquid and separated by centrifugation. The resulting powders hereafter named as $\text{Zn}_2\text{Al/LS}$ was washed several times with distilled water and finally dried at room temperature. Two other LDH compositions were synthesized in similar condition using Mg:Al (2:1) and Co:Al (2:1) and pH coprecipitation value of 10 ± 0.1 and 8 ± 0.1 , respectively.

2.3. Preparation of the biodegradable polymer nanocomposite

Prior to their preparation, the three polyesters were dried at 40°C for 48 h in air oven, while $\text{Zn}_2\text{Al/LS}$ organoclay was dried at 100°C for 2 h. The three thermoplastic polyesters were melt-processed on a standard micro-extruder equipment at 170°C (5'), 120°C (5') and 140°C (10') in a twin screw extruder (rotation 100 rpm) for PLA, PBS and PBAT, respectively. Organoclay loading was of 5 wt.%. For further analyses, polymer films were prepared by hot pressing.

2.4. Characterization

Elemental analysis (S, Al and Zn) was performed at the Vernaison Analysis Center of CNRS using inductive conduction plasma coupled to atomic emission spectroscopy (ICP/AES). The chemical compositions were reported from elemental analyses, Zn, Al, S at.%.

XRD analyses of the hybrid LDH and polymer nanocomposites were performed on a Siemens D501 diffractometer using $\text{Cu K}\alpha$ source (30 mA, 35 kV); data were collected in a step scan mode between 2.0 and $70.0^\circ(2\theta)$ and with a step size of $0.03^\circ(2\theta)$ and a

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