



Preparation and properties of blends composed of lignosulfonated layered double hydroxide/plasticized starch and thermoplastics



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ABSTRACT

Layered double hydroxide prepared with lignosulfonate (LDH/LS) can be easily dispersed down to the nanometric scale in thermoplastic starch, at concentration of 1 up to 4 wt% of LDH/LS. They can thus be used as a bio-based reinforcing agent of thermoplastic starch. Incorporation of LDH/LS in starch must be done using LDH/LS slurry instead of powder in order to avoid secondary particles aggregation, the water of the paste being used as the starch plasticizer. This reinforced starch was used for preparing a starch–polyolefine composite. LDH/LS–starch nanocomposites were mixed in a random terpolymer of ethylene, butyl acrylate (6%) and maleic anhydride (3%) at concentrations of 20 wt% and 40 wt%. With a 20% loading of (1 wt% LDH/LS in thermoplastic starch), the ternary copolymer is partially bio-based while keeping nearly its original processability and mechanical properties and improving oxygen barrier properties. The use of layered double hydroxides is also removing most odours linked to the lignin phase.

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1. Introduction

Starch has been extensively studied as a structural or functional polymer because of its renewability, abundance and biodegradability. A major breakthrough was the discovery of its thermoplasticity when processed with a low content of water or plasticizer, at elevated temperature and under mechanical action (Forsell, Mikkilä, Moates, & Parker, 1997). This opened the way to prepare starch-based polymer blends that are now commercially used for a variety of applications like biodegradable packaging films. During the processing used for preparing thermoplastic starch, the native granular structure of starch is destroyed and amylose and amylopectin are dispersed and more or less randomly distributed in the medium, leading to an amorphous thermoplastic material that can recrystallise with time, but with crystalline structures different from the ones present in native starch granules (Bastioli, 1998; Van Soest & Esser, 1997). However, thermoplastic starch is suffering several drawbacks, the most important ones being its poor mechanical properties and its sensitivity to water (Chaléat, Halley, & Truss, 2008; Follain, Joly, Dole, & Bliard, 2005). When the sensitivity to moisture must be decreased, starch can be embedded

in a matrix composed of a hydrophobic polymer. Regarding mechanical properties, brittleness is decreased by the addition of a plasticizer like water or glycerol, but this is degrading its mechanical strength. To improve the low mechanical tensile properties, a classical strategy consists on including soft or rigid small particles. One possibility which has been widely studied is the use of nanosized particles. Such nanocomposites have met a wide range of applications in environmental (i.e. catalytic degradation, detection of contaminants) (Zhao et al., 2011), optical (i.e. OLED, photovoltaic cells) (Nguyen, 2011), biomedical (Armentano, Dottori, Fortunati, Mattioli, & Kenny, 2010) or packaging (Tang, Kumar, Alavi, & Sandeep, 2012) sectors. One advantage of nanocomposites is the low content of fillers (less than 5 wt%) needed to match the properties of conventional composites with much higher loadings. Nanoscale fillers have a much higher surface area than conventional fillers, increasing enormously the interactions between filler and polymer matrix (Chivrac, Kadlecova, Pollet, & Avérous, 2006). Nanocomposites can be used to prepare light composites having large modulus, low permeability, good thermal stability or transparency. Nanofillers have at least one dimension in the nanometric range, like clay, carbon nanotubes, graphene, or cellulose nanowhiskers. Depending of process conditions and affinity between fillers and matrices, different states of dispersion can be obtained: (a) phase separated with aggregates called microcomposite, (b) intercalated where layers are uniformly dispersed but remain ordered and (c) exfoliated when filler is fully and uniformly dispersed and completely disoriented. Exfoliated structures are

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always the ultimate goal in nanocomposite compounding since the best performances especially concerning barrier properties should be obtained (Vaia & Giannelis, 1997).

Starch filled with nanostructures has been studied in order to improve mechanical stiffness, barrier properties and to reduce flammability. Various types of inorganic layered fillers such as montmorillonite (Park et al., 2002), hectorite (Chen & Evans, 2005), kaolin (Carvalho, Curvelo, & Agnelli, 2001) or layered double hydroxide (Wu, Chang, & Ma, 2011) have been tried. Storage modulus of starch nanocomposites was found to be in the following order, with the best results obtained for kaolinite: kaolinite > brucite > hectorite > layered double hydroxide (Wihelm, Sierakowski, Souza, & Wypych, 2003a). Property improvement is very much dependent on the possibility to obtain a good dispersion of nanofillers and a good interfacial adhesion between fillers and matrix. However, it was reported that clay is difficult to be dispersed in starch (Bagdi, Muller, & Pukanszky, 2006; Chiou et al., 2006; Park, Lee, Park, Cho, & Ha, 2003). It was also reported that glycerol, used as a starch plasticizer, had the tendency to penetrate clay fillers leading to non exfoliated structures (Wihelm, Sierakowski, Souza, & Wypych, 2003b). To improve the dispersion of nanofillers into the starch matrix, the counter anion should be compatible with starch (Chivrac, Pollet, Schmutz, & Avérous, 2008). Pandey and Singh (2005) studied different methods to prepare starch–clay nanocomposites, the best intercalation results being obtained with the incorporation of the plasticizer after mixing starch with clay since polymer chains can then migrate inside the clay galleries before the plasticizer molecules.

Among the family of clay nanofillers, layered double hydroxides (LDH) present the advantage to be highly versatile with many options for choosing the anionic organic interlayer molecules, giving a large variety of LDH hybrid materials (Leroux, 2006). Although LDH can be found in nature, they can also be synthesized to fulfil specific requirement at relatively low cost (Utracki, Sepehr, & Boccaleri, 2007). Layered double hydroxides are based on positively charged brucite-like sheets formed by the substitution of divalent to trivalent cations, leading to a positive charge sheet counterbalanced by the presence of an anion in the interlayer space. A previous study show that it is possible to use a widely available by-product of the pulp industry, lignosulfonate, as the organo-modifying molecule intercalated into layered double hydroxide (Hennous et al., 2013), having in mind that such formed fillers are environmentally-friendly since MgAl-hydrotalcite is typically envisioned for drug delivery (Costantino, Nocchetti, Tammaro, & Vittoria, 2012) and as a gene reservoir (Oh, Park, Choi, & Choy, 2012). Recently reported to organo-modify LDH platelets, alginate (another bio-related polymer) was found to improve the detection sensitivity of sensor-based systems (Sanchez-Paniagua Lopez, Leroux, & Mousty, 2010) and the ion conductivity for polymer electrolytes (Leroux, Chabrol, Morlat-Théris, Gardette, & de Roy, 2012). Lignosulfonate are water-soluble anionic polyelectrolyte polymers obtained in large quantities. When not burned, they are mainly used in making concrete for superplasticizing effect, in drilling fluids, and as dispersants in various applications.

The aim of the present study is to study the preparation of layered double hydroxide/lignosulfonate (LDH/LS)-reinforced thermoplastic starch/polyethylene based polymer blends and to evaluate their interest, mainly considering gas barrier and mechanical properties.

2. Experimental

2.1. Materials

Native corn starch was provided by Novamont (Italy). Calcium lignosulfonate was kindly supplied by Tembec (France) as a brown

powder with a calcium content of 3% dry matter. Glycerol was an analytical grade purchased from Sigma–Aldrich. Lotader 3210 is a random terpolymer of ethylene, butyl acrylate (6%) and maleic anhydride (3%) produced and kindly given by Arkema (France).

2.2. Preparation of LDH–lignosulfonate (LDH/LS)

LDH composition is Zn₂Al and is prepared by a co-precipitation method as explained in a previous article (Hennous et al., 2013). The prepared LDH/LS mixture was kept in slurry form with 18% dry matter.

2.3. Preparation of LDH/LS–thermoplastic corn starch (TCS)

Corn starch powder was first dried overnight at 70 °C under vacuum to remove the free water (~10 wt% of the material). The content of glycerol was fixed at 35 wt% based on dry starch. Water is used as co-plasticizer in the range of 15 wt%. The filler loading levels of LDH/LS were 0, 1, 2, and 4 wt% based on dry starch. The preparation of the thermoplastic starch mixture with glycerol and LDH/LS was performed in two steps. In the first step, a quantity of LDH/LS mixture was dispersed into glycerol using vigorous magnetic stirring until complete dispersion of LDH/LS. Corn starch was then mixed manually with the obtained plasticizer–nanofiller mixture. In the second step, the total glycerol–starch–LDH/LS–water mixture was sheared in an internal mixer Haake Rheomix 600 equipped with roller rotors at 90 °C and 100 rpm for 20 min. The LDH/LS–plasticized starch blends were injection moulded into tensile test specimens using a MiniJet apparatus from ThermoFisher at 160 °C, with the mould at 50–65 °C and injection pressure of 300–600 bars. Specimens were kept in a conditioning room at 20 °C and 55% relative humidity before characterization. Part of blends was kept as granulates for further blending with the Lotader thermoplastic and the other part was used to prepare test specimens for X-ray scattering were compression moulded into pieces of 50 mm × 50 mm × 2 mm.

2.4. Preparation of Lotader-thermoplastic reinforced with LDH/LS–TCS

LDH/LS–TCS granulates obtained as described previously and Lotader 3210 were dried overnight at 50 °C under vacuum. Lotader/(LDH/LS–TCS) nanocomposites were blended in an internal mixer Haake Rheomix 600 equipped with roller rotors at 140 °C and 100 rpm for 10 min. Loadings of LDH/LS–TCS nanocomposites into Lotader 3210 matrix were 20 and 40 wt%. The blends were then compression moulded and (1) cut as tensile test specimens ISO 527-1BA, or (2) into 20 mm circular specimens of 2 mm thickness for rheology measurements, or (3) cut as test samples of 50 mm × 50 mm × 2 mm for water sensitivity measurement, or (4) formed as 100 mm circular films of 400 μm thickness for O₂ permeability measurements.

2.5. Characterization

2.5.1. Odour and volatile compound analyses

Odour and volatile organic compounds were determined with an electronic nose HERACLES from Alpha M.O.S. (France). HERACLES electronic nose is equipped with two columns (DB5 apolar and DB1701 slightly polar), 2 m length and 100 μm in diameter. Calibration was done with alcane from *n*-hexane to *n*-hexadecane. Data treatment was done with Alphasoft V12.3 software using AroChem-Base database. Table 1 gives the parameters of analysis used for lignosulfonate and lignosulfonate interleaved into Zn₂Al layered double hydroxide.

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