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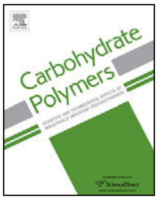

Fabrication and characterization of novel starch-grafted poly L-lactic acid/montmorillonite organoclay nanocomposites

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ABSTRACT

In this work, poly(L-lactic acid)-*g*-starch layered silicate nanocomposites (NCs) (PLLA-*g*-starch/MMT) were fabricated by intercalative bulk graft copolymerization of LA with starch, in the presence of either stannous octoate acting as a catalyst or LA-MMT organoclay acting as a cocatalyst-nanofiller. This procedure was performed inside a custom vacuum micro-reactor. To better understand the graft copolymerization mechanism, in situ processing types, interfacial interactions and nanostructure formation of PLLA-*g*-starch/MMT NCs, methods such as FT-IR, XRD, ^{1}H NMR, ^{13}C CP/MAS-NMR, DSC/TGA, TEM and SEM were utilized. The morphology and thermal behaviors of nanocomposites were found to be strongly dependent on the loading mass fraction of LA-MMT within the nanocomposite structure and the type of in situ processing such as interfacial, physical and chemical interactions. Preintercalated LA-MMT organoclay exhibited dual functions. It demonstrated the ability to act as a catalyst, essentially accelerating in situ graft copolymerization via esterification of LA carboxyl groups with hydroxyl groups of starch macromolecules, whilst also acting as a nananofiller-compatibilizer.

1. Introduction

Commodity polymers are non-degradable materials which may be discarded in a short time leading to ecological and environmental concerns (Bertuzzi, Armada, & Gottifredi, 2007). Recently, concerns regarding the environmental impacts have resulted in an ever-increasing shift of global energy policies pertaining to the replacement of sustainable sources of value-added and environmentally friendly products.

Natural polymers, including those based on polysaccharides, have offered a solution for polymer scientists attempting to overcome the conventional plastics waste disposal problem (Cinelli, Chiellini, Lawton, & Imam, 2006; Durango et al., 2006; Fairley, Monahan, German, & Krochta, 1996; Fang et al., 2005; Gennadios, 2002; Kester & Fennema, 1986; Krochta & De Mulder-Johnston, 1997; Sebti, Ham-Pichavant, & Coma, 2002; Shahidi, Arachchi, & Jeon, 1999; Weber, Haugaard, Festersen, & Bertelsen, 2002).

Starch is considered to be a very important renewable resource for biodegradable polymeric materials (Petersen et al., 1999; Yu, Chang, & Ma, 2010; Zobel, 1988). However, the poor compatibility of polysaccharides (starch, cellulose, etc.) with synthetic polymers (polyolefins) limits the production of composite blends. There is much literature about the blending of starch with natural and commodity polymers (Otey & Westhoff, 1982). However, the hydrophilic structure of starch is known to create a weak interfacial interaction between itself and hydrophobic polymers such as PLA, Poly caprolactone (PCL) or polybutylene adipate-co-terephthalate (PBAT), resulting in poor mechanical properties of the final blend (Mittal, Akhtar, & Matsko, 2015).

Grafting of hydrophobic thermoplastic polymers with more hydrophilic monomers (e.g., maleic anhydride (MA) and dioctyl maleate (DOM)) has been proposed as an effective approach to solving incompatibility issues, allowing the fabrication of compatible and biodegradable polymeric blends (Rzayev, 2010, 2011). MA has been previously used a nontoxic reactive compatibilizer to improve not only compatibility but also other properties of poly(lactic acid) (PLA)/starch blends used for extrusion processing (Zhang & Sun,2004).

Considering the effects of such compatabilizers we developed, in a previous study, a new green approach to overcoming the processing difficulties of starch involving the graft

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copolymerization of poly L-lactic acid onto starch in the presence of supercritical carbon dioxide as a reaction medium (Salimi, Yilmaz, Rzayev, & Piskin, 2014).

PLA, with a linear aliphatic polyester structure, is one of the most important biobased polymers derived from renewable sources, exhibiting a combination of physical properties and features which make it a good alternative to petrochemical resources (Nuona, Xianye, Xiaoshu, Yinghong, & Jianfei, 2015). Insufficiencies in mechanical and thermal properties of most natural polymers translate to processing difficulties and therefore impede the ability to mass produce environmentally friendly products. Adding nanofiller materials to natural and synthetic polymers or their products, improves both physical properties (thermal stability, flame-retardance, barrier properties, etc.) and mechanical properties of PLA based polymers. The most frequently used filler material in the production of nanocomposites is silicates (monmorillonite, hectorite, saponite, fluoromica, fluoro hectorite, vermisulite, caolinite, etc.). The most common layered silicate used for PLLA is montmorillonite (Miyoshi, Hashimoto, Koyanagi, Sumihiro, & Sakai, 1996; Nam, Fujimori, & Masuko, 2004; Paul et al., 2005; Pluta, Paul, Alexandre, & Dubois, 2006; Rzayev, Salimi, Eğri, & Pişkin, 2014; Salimi, Rzayev, & Pişkin, 2014; Shibata, Someya, Orihara, & Miyoshi, 2006; Tanoue, Hasook, Iemoto, & Unryu, 2006). These, silicate layers are expected to be highly exofliated in order to improve the mechanical properties of polymer/clay nanocomposites. To obtain clay/polymer nanocomposites with desired properties better attraction between the polymer and organo-modified clay (gap between silicate layers expand with organic cations) is required (Hofmann, 1968). Homogenous distribution of clay within the matrix is achieved through the increased clay – polymer interaction. The most common process used for organo-modified clay preparations is ion exchange with alkyl ammonium cations which contain various groups. Cyras et al. studied the effect of montmorillonite on the physical and mechanical properties of glycerol-plasticized starch/clay nanocomposite films, where the intercalation of the clay was without complete exfoliation in the nanocomposite (Cyras, Manfredi, Ton-That, & Vázquez, 2008). Wokadala, Ray, Bandyopadhyay, Wesley-Smith, and Emmambux (2015) have reported the effect of various nanoclays on PLA/butylated-starch nanocomposites prepared via melt blending. They found that the morphological and thermal properties of the blend nanocomposites were related to the hydrophobicity of the nanoclays (Wokadala et al., 2015). They also investigated the effects of several other factors, such as extrusion papameters, starch/clay nanocomposite melt intercalations and clay content, clay cation type, clay dispersion techniques and different starch resources, on physical and mechanical properties (Chen & Evans, 2005; Chiou, Yee, Glenn, & Orts, 2005; Cyras et al., 2008; Dean, Yu, & Wu, 2007; Mondragon, Mancilla, & Rodriguez-Gonzalez, 2008; Park, Lee, Park, Cho, & Ha, 2003; Wilhelm, Sierakowski, Souza, & Wypych, 2003). Ayana et al. synthesized thermoplastic starch (TPS)/polylactic acid (PLA)/sodium montmo-rillonite (NaMMT) nanocomposites via melt mixing of PLA/TPS/nanoclay nanocomposites and investigated the effects of nanoclay compatibilizer on the properties of nanocomposites (Ayana, Supratim, & Khatua, 2014). Unlike our applied method in this study, Namazi et al. were used two step reactions such as (1) reaction of starch with LA and (2) solution intercalating of acetylated starch with inorganic Na^+-MMT clay. Furthermore, they used three types of clays including inorganic mineral clay (Na^+-MMT) and its two reactive organic derivatives as nanofillers with different action mechanisms (Namazi & Belali, 2015).

In this study, we have demonstrated intercalative graft copolymerization of LA onto starch in the presence of LA-MMT organoclay to produce PLLA-g-starch/MMT NCs. The composition–structure–property relationships of the nanocomposites were evaluated by chemical, physical, thermal, and morphological analysis in order to help gain a better understanding of the formation of nanostructures, interfacial interaction, in situ processing, and properties.

2. Experimental

2.1. Materials

The two main resources used in this study were natural corn starch (28% amylose, 72% amylopectin, Cargill, USA) and L-lactic acid solution (20% aqueous solution, PURAC, The Netherlands). NaOH (Merck, Germany), dimethyl sulfoxide (DMSO) (Merck, Germany), stannous octoate ($Sn(Oct)_2$) (Sigma Aldrich, USA), pristine montmorillonite (MMT) clay (Na^+-MMT) (Sigma Aldrich, USA), were used as received.

2.2. Manufacturing

The synthetic pathway for the preparation of the LA-MMT nanofillers (NC-1) and PLLA-g-starch/MMT (NC-2) nanocomposites includes a two-step reaction that is schematically demonstrated as follows (Figs. 1 and 2): at first, the pre-intercalation of pristine-MMT fillers was performed in the presence of L-lactic acid. For this, the clay (Na^+-MMT) was dispersed in LA by intensive mixing at room temperature for 12 h until the intercalation of LA monomer between silicate interlayer species was achieved (Fig. 1A). For the complete intercalation of LA monomers between silicate galleries, interlamellar bulk polymerization of L-LA was carried out by condensation polymerization using different ratios of L-LA to preintercalated MMT and/or pristine MMT with a double neck balloon reactor at 90 °C for 9 h under vacuum (Fig. 1B).

Graft copolymerization of starch and LA-MMT was performed as reported in our previous study (Fig. S1) (Salimi, Yilmaz, Rzayev, & Piskin, 2014). Briefly, corn starch was gelatinized with a 0.4 M solution of NaOH in a three necked reactor at 70 °C for 1 h. The graft copolymerization was initiated by combining a L-LA-MMT mixture (with 3.0% (by weight), nanofiller complexes prepared previously with pristine MMT by 1.5, 3.0 and 4.5% (by weight) ratios), a catalyst ($Sn(oct)_2$) and dimethyl sulfoxide (DMSO), for 10 h under vacuum (−600 mmHg) conditions. After the specified conditions were fulfilled, the product was washed twice with methanol to remove the unreacted LA and oligo(lactic acid). Finally, the extracted PLLA-g-starch/MMT (NC-2) NCs were dried at 70 °C under vacuum.

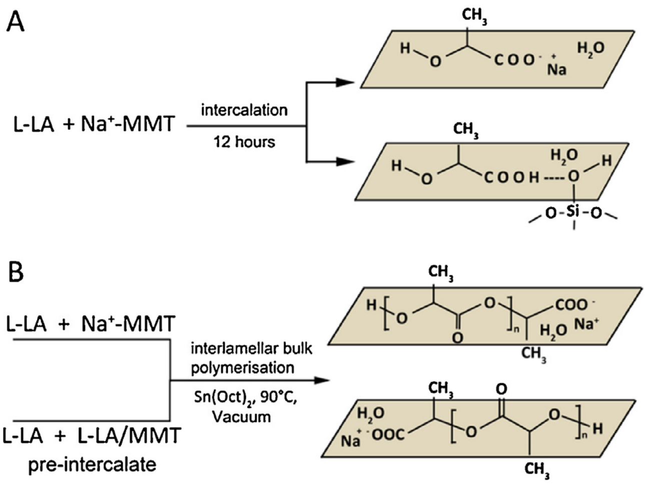

Fig. 1. Increasing the distance between MMT galleries; (A) by pre-intercalation; (B) by polymerization using L-LA and pristine MMT or L-LA/MMT pre-intercalate (NC-1).