Industrial Crops and Products 77 (2015) 833–844

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Effect of lignin nanoparticles and masterbatch procedures on the final properties of glycidyl methacrylate-*g*-poly (lactic acid) films before and after accelerated UV weathering

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ARTICLE INFO

Article history:
Received 7 June 2015
Received in revised form
21 September 2015
Accepted 23 September 2015
Available online 22 October 2015

Keywords:
Poly (lactic acid)
Lignin nanoparticles
Nanocomposites
Masterbatch
Grafting

ABSTRACT

This article reports the preparation, by means of an innovative masterbatch procedure, of poly (lactic acid) (PLA)/lignin nanoparticles (LNP) films via premixing 1% wt. of LNP into PLA or glycidyl methacrylate (GMA) grafted PLA (g-PLA). These films were obtained by reactive extrusion and subsequent filmature process. Films obtained by using the masterbatch steps were characterized and compared with the system realized by direct extrusion of 1% wt. of LNP in PLA/g-PLA. Thermal, optical and mechanical properties, as well as morphology of LNP reinforced PLA nanocomposites, were characterized. The performance of the produced films was also investigated after accelerated UV weathering (up to 480 h), with the aim of verify how the presence of lignin nanoparticles could modify transparency and mechanical performance of neat (and GMA grafted) PLA films. Results from UV–vis characterization showed how LNP better behave as UV light barrier in grafted PLA, and it has been also proved that GMA grafting onto PLA matrix promoted the dispersion of LNP in matrix. Mechanical tests after weathering also confirmed that both the presence of LNP and GMA accelerates the oxidation effect, since the increased deformability observed for systems containing 1% wt. of LNP in PLA and g-PLA systems at time 0 was lost after 240 h of UV exposure.

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1. Introduction

Lignin, as the second most abundant renewable and biodegradable natural resource next to cellulose, is a highly-branched, three dimensional biopolymer. It is a complex macromolecule, based on the repetition of three different phenylpropane units (*p*-coumaryl, coniferyl and sinapyl alcohols, linked together by ether or CC bonds). Many functional groups (carbonyl, phenolic or aliphatic hydroxyls, carboxyl, etc.) can be found in different proportions in lignin, and the molecular weight can range from thousand to several tens of thousands (Boeriu et al., 2004; Baumberger et al., 2007; El Mansouri and Salvadó, 2007). The abundance of functional groups on lignin surface is one of the reasons why it is widely studied as reinforcing filler for plastics and rubber. These functional groups provide scope for chemical modification and polarity adjustment to produce compatibility with appropriate polymeric matrices (Frigerio, 2014). In addition, these merits make lignin attractive for development of polymer composites (Bahl et al., 2014).

There is a trend, in food packaging industry, that renewable plastics will substitute petroleum based plastics with lower environmental impact. Among them, poly (lactic acid) (PLA) is a very promising material because of its interesting physical and functional properties, low cost and commercial availability. Although PLA possesses good melt processability, it exhibits some limitations when used in food applications (high brittleness, slow crystallization rate and relatively low thermal and mechanical properties), in comparison to equivalent traditional polymers. In order to increase its potential in the fabrication of attractive materials for wide industrial applications, many research studies have focused on overcoming these limitations (Jamshidiana et al., 2012; Jonoobi et al., 2010). In this context, the addition of nanoparticles as polymer additives positively contributes to enhance the gas barrier, due to the synergistic tortuosity, crystal nucleation and chain immobilization effects (Fortunati et al., 2014; Martino et al., 2010). Indeed, lignin has been studied as ultraviolet (UV) absorbent (Toh et al., 2005; Chung et al., 2013). Thakur et al. (Thakur et al., 2014) recently reviewed and discussed the use of large size lignin in thermoset, thermoplastic, elastomer based composites and foamed materials. However, poor dispersion of lignin in many composites was observed and attributed to its propensity to self-aggregate. Some methods were attempted to improve the dis-

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http://dx.doi.org/10.1016/j.indcrop.2015.09.057
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persion of lignin particles in PLA matrix. Indication of how lignin particles (in their microscopic dimension) behave when included in PLA is reported in Domenek et al. (Domenek et al., 2013), in which the authors investigated the migration of low molecular weight compounds in an ethanol/water solution simulating fatty foodstuff. In that specific case, it was found that the migration from the PLA-lignin films with only 1 wt% of inclusion was not significant. In a study by Chung et al. (Chung et al., 2013), it is reported that graft polymerization of lactide onto lignin catalyzed by triazabicyclodecene (TBD) resulted in a lignin-g-PLA copolymer, in which the chain length of the PLA is controlled by varying the lignin/lactide ratio and using a pre-acetylation treatment. End group analysis revealed high grafting efficiency and preferential grafting on lignin aliphatic hydroxyls over phenolic hydroxyls. The lignin-g-PLA copolymers displayed a glass transition temperature ranging from 45 to 85 °C and multiphase melting behavior. In this case, lignin-g-PLA copolymers were also used as dispersion modifiers in PLA based materials to enhance UV absorption and increase the tensile strength and strain, without a sacrifice in the modulus of elasticity. Gordobil (Gordobil et al., 2014) produced PLA/acetylated lignin blends, which exhibited greater compatibility than non acetylated PLA/lignin. Acetylated lignins had lower T_g and higher thermal stability than original lignins, but a limitation in the PLA crystallization was indeed observed. PLA/acetylated lignin blends remained fairly constant in strength even at high percentages, and the elongation at break also increased. Ouyang et al. (Ouyang et al., 2012) prepared PLA based ternary blends consisting of PLA, cellulolytic enzyme lignin (CEL), and polyolefin grafting maleic anhydride (PGMA) by extrusion. Scanning electron microscopy observations revealed that the CEL plays a bridging role between PLA and PGMA, enhancing the miscibility between them and resulting in the improvement of ductility and toughness of the ternary blends. In order to compatibilize lignin with PLA, Eyser (Eyser et al., 2011) successfully synthesized lignin and PLA via solution polymerization to form a renewable copolymer after lignin butylation. Sun et al. (Sun et al., 2015) fabricated PLA-lignin composites by blending lignin-g-rubber-g-poly (D-lactide) copolymer particles and commercial poly (L-lactide) (PLLA) in chloroform (masterbatch). The rubbery layer made of poly (ϵ-caprolactone-co-lactide) (PCLLA) was formed via lignin-initiated ring opening copolymerization of ϵ-caprolactone/L-lactide mixture, followed by the formation of poly (D-lactide) (PDLA) outer segments via polymerization of D-lactide. The resulting renewable and biodegradable composites exhibited a six-fold increase of elongation at break and a simultaneous improvement of tensile strength and Young's modulus albeit to a lesser extent. The obtained results suggested that good lignin dispersion, rubber initiated crazing and strong filler-matrix interactions due to stereocomplexation are the effective mechanisms behind the excellent mechanical performances. Even if this method seemed to be effective for good dispersion of lignin into PLA matrix, it is certainly complicated and costly.

The possibility of using easy processing methods was indeed considered in our proposed approach: specifically, in this study, we highlight the simplified fabrication of stable and uniformly distributed lignin nanoparticles (LNP) premixed (1% wt.) in different masterbatches based on PLA or modified PLA matrix (glycidyl methacrylate melt grafted PLA) and finally processed into films. The use of a masterbatch approach has been confirmed to be an effective solution to enhance the performance of resulted PLA nanocomposites, as reported in our previous study (Pracella et al., 2014), in which cellulose nanocrystals (CNC) were selected as nanofillers. To the best of our knowledge, no results have been reported so far regarding a similar approach in the case of nanosized lignin based materials. Thermal, optical and mechanical properties were tested and reported here, with the aim of evaluating their suitability in the food packaging sector. A further aim was the optimization of approaches suitable to process the nanocomposites, providing a novel reference for industrial manufacturing and practical application of bioplastic based nanocomposites reinforced by LNP. The performance of the produced films was also investigated after an accelerated UV weathering, in order to test how the presence of lignin nanoparticles could modify transparency and mechanical performance of neat (and GMA grafted) PLA films realized by using the masterbatch procedure.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA 3251D), with a specific gravity of 1.24 g/cm^3, a relative viscosity of ca. 2.5, and a melt flow index (MFI) of 35 g/10 min (190 °C, 2.16 kg) was supplied by NatureWorks LLC, USA. Glycidyl methacrylate (GMA), with a density of 1.042 g/mL at 25 °C, and dicumyl peroxide (DCP), with a density of 1.56 g/mL at 25 °C, were supplied by Sigma-Aldrich. PLA pellets were dried in an oven at 40 °C overnight. Pristine lignin, obtained as bio-residue of conversion of *Arundo donax* L. biomass to bioethanol in a steam explosion pretreatment, followed by enzymatic reactions and filtration, was supplied by CRB (Centro Ricerca Biomasse, University of Perugia) (Cotana et al., 2014).

2.2. Methods

2.2.1. Lignin nanoparticle (LNP) synthesis and characterization

LNP suspension was prepared from pristine lignin by hydrochloric acidolysis presented in our previous study (Yang et al., 2015a). The LNP were examined by a field emission scanning electron microscope (FESEM, Supra 25-Zeiss) with an operating voltage at 5 kV. Few drops of the LNP suspension were cast on to silicon substrate, dried for 24 h and gold sputtered before the analysis.

2.2.2. Preparation of masterbatches (MBs)

In order to determine the effects of processing procedures on the properties of the PLA based nanocomposites, we fixed the content of LNP and PLA grafted with GMA (g-PLA) in the resulted nanocomposites at 1% wt. and 15% wt., respectively. The content of the compatibilizer was selected on the basis of literature papers (Liu et al., 2012; Thanh et al., 2015), taking into consideration how the content of grafted GMA can be varied as a function of GMA in the feed. In the case of lignin nanoparticles content, 1% wt. of LNP was taken as suitable for a preliminary investigation, on the basis of our previous results obtained in the case of extruded PLA films containing 1% wt. of CNC, realized by means of analogous masterbatch procedure (Yang et al., 2015b). Grafting of GMA onto the PLA was performed in a twin-screw microextruder (DSM Explorer 5&15CC Micro Compounder) in the presence of DCP as initiator. Before being used for grafting, GMA was stored in the refrigerator at 5 °C. DCP content was set as 1 wt% of the PLA weight, while GMA was fixed at 10% wt. of the PLA weight. DCP and GMA (DCP/GMA ratio = 0.1) were mixed and the obtained solution was sprayed onto dried PLA matrix. The mixture of GMA, PLA and initiator DCP was then introduced into the microextruder: mixing screw speed of 100 rpm and mixing time of 8 min were used in order to realize the grafting reaction, while a temperature profile of 165–175–180 °C was selected. GMA grafting was confirmed by means of FTIR analysis, and the final grafting degree was evaluated as 5.7% (Yang et al., 2015b).

The different masterbatches were obtained by mixing various amounts of LNP with PLA or g-PLA (Fig. 1). In details, the following processing conditions were applied:

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