Industrial Crops and Products 72 (2015) 159–165

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Ternary melt blends of poly(lactic acid)/poly(vinyl alcohol)-chitosan

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ARTICLE INFO

Article history:
Received 28 August 2014
Received in revised form
16 December 2014
Accepted 21 December 2014
Available online 6 January 2015

Keywords:
Polymer blend
Melt blend
Chitosan
Poly(vinyl alcohol)
Poly(lactic acid)

ABSTRACT

Chitosan has aroused considerable interest because of its antimicrobial activity and biocompatibility and its use in functional blends with antimicrobial properties is growing, but it is still very limited since it cannot be melted under normal conditions and there is some doubt about the actual morphology of the purported blends. Here, we described a novel technique for melt processing chitosan in a blend with poly(lactic acid) and poly(vinyl alcohol), the latter being used as compatibilizing agent and the entire system being plasticized with a mutual plasticizer, glycerol. Blends were clear and the image of the brittle fracture surfaces shows a chitosan/PVA dispersed phase, of size varying from 0.5 to 2.5 μm, in the PLA phase. This paper presents for the first time a melt blend in which the chitosan phase is not distributed as particles in a composite and opens a new field of investigation of functional bioactive polymer blends.

1. Introduction

The development of new biodegradable plastics such as chitosan which exhibit inherent antimicrobial activity is considered of great importance in several areas, including packaging (Bordenave et al., 2010), textiles (Kumar, 2000) and biomedical applications (Muzzarelli and Muzzarelli, 2005). Chitosan, a copolymer of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose units joined by $\beta(1 \rightarrow 4)$ bonds, is obtained by alkaline deacetylation of chitin, one of the most abundant biopolymers. Chitosan is biodegradable, non-toxic to humans and has excellent film-forming ability, which makes it a truly promising material; however, it is not in widespread use, since it cannot be processed by melting techniques as most commercial plastics. Despite claims in the literature that melt blends of chitosan have been developed (Correlo et al., 2005a,b), it is used more as a filler that does not melt during processing. In reality, apart from its use as a filler, chitosan can only be processed from its solution in water, in the presence of acids (Sarasam et al., 2006; Huang et al., 2005), and in costly and complex organic solvents such as 1,1,1,3,3,3,-hexafluoro-2-propanol/2,2,2-trifluoroethanol mixtures (Cai et al., 2010) and ionic liquids (Sun et al., 2013). This fact limits not only the processing of these materials but also the possibility of combining chitosan with other polymers to form polymer blends, which is one of the most versatile ways of producing new plastics from existing polymers. In a previous paper (Grande and Carvalho, 2011), we used the emulsion blending technique to prepare blends of chitosan with a non-water-soluble polymer, poly(lactic acid) (PLA). Poly(vinyl alcohol) (PVA) was used as compatibilizer. PLA is a biodegradable polymer, whose annual production reaches 140,000 metric tons a year, it being (Shah et al., 2008) one of the first commercially successful biodegradable polymers (Auras et al., 2004). The composition of this ternary blend of chitosan/PLA/PVA was based on the fact that PVA can form miscible blends with chitosan and that these are compatible with PLA. The interest in the use of PLA arise not only from its biodegradable character but also from the fact that it can be used in the production of fibers, extruded films and injection-molded products that can be used in a great number of biomedical, (Fen et al., 2009) engineering (Jiang et al., 2006) and special textiles applications, among others (Gupta et al., 2007). Blends developed from chitosan and PLA can combine in a single material the antimicrobial activity of chitosan and the easy processing and interesting physical properties of PLA. Nevertheless, two main drawbacks to producing these blends need to be overcome: (i) chitosan does not melt in conventional processing techniques and (ii) chitosan and PLA are incompatible because of their differences in polarity.

Here, the use of PVA to compatibilize chitosan and poly(lactic acid) was investigated further. However, in the present study, rather than processing by emulsion blending, melt blending was used and glycerol, a common plasticizer for chitosan (Nugraha et al., 2005), PLA (Martin and Avérous, 2001) and PVA (Alexy et al., 2003), was introduced. Glycerol would not only increase the compatibility

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http://dx.doi.org/10.1016/j.indcrop.2014.12.041
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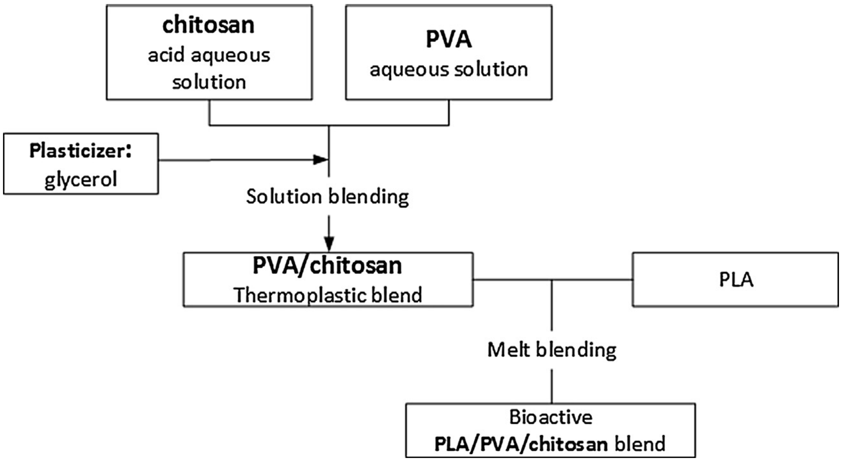

Scheme 1. Flow diagram of the process used to produce melt blends of chitosan with other polymers.

of the components but also decrease the processing temperature of the PVA/chitosan miscible blend (Alexy et al., 2003).

In short, in this study, we prepared a ternary blend of PLA/chitosan and PVA by melt processing. The strategy adopted was to produce a miscible blend of PVA/chitosan plasticized with glycerol by solvent blending, and then melt blend the PVA/chitosan blend with PLA to produce a ternary two phase blend. The process is based on the dissolution of chitosan into PVA and the dispersal of this thermoplastic blend into a PLA matrix. This process is shown schematically in Scheme 1. To our knowledge, this is the first description of a melt blend containing chitosan where the chitosan phase behaves as a melt.

2. Materials and methods

2.1. Materials

Chitosan with approx. 85% deacetylation, intrinsic viscosity 0.328 L/g (in 1% acetic acid solution at 25 °C) and molecular weight 60,100 g mol^{-1} (viscometric); PLA from Nature Works (PLA 2002d), with molecular weight M_n = 92,000 mol^{-1} and M_w = 150,000 g mol^{-1}, and PVA from Sigma–Aldrich (cat. # 360627), with M_w 9000–10,000 g mol^{-1} and degree of hydrolysis 80%. Glycerol and acetic acid were reagent grade and used as received.

2.2. Solution blending of PVA-chitosan

Chitosan and PVA were blended by mixing a 1% solution of PVA in water with a 1% solution of chitosan in 1% aqueous acetic acid. Glycerol was added to this mixture so that the final proportions of chitosan/PVA/glycerol were 9:82:9, 22.7:68.3:9 and 45.5:45.5:9. The resulting solution was dried in a forced air oven at 38 °C for 72 h and then dried in a vacuum oven for 24 h at 50 °C. The chitosan/PVA glycerol-plasticized blend was cryogenically ground. The resulting powder was then dried under vacuum for 24 h at 50 °C.

2.3. Melt blending of PLA/PVA-chitosan

Powdered PVA-chitosan blends were mixed with PLA pellets in the proportion PLA/PVA-chitosan-blend of 75:25. The mixtures

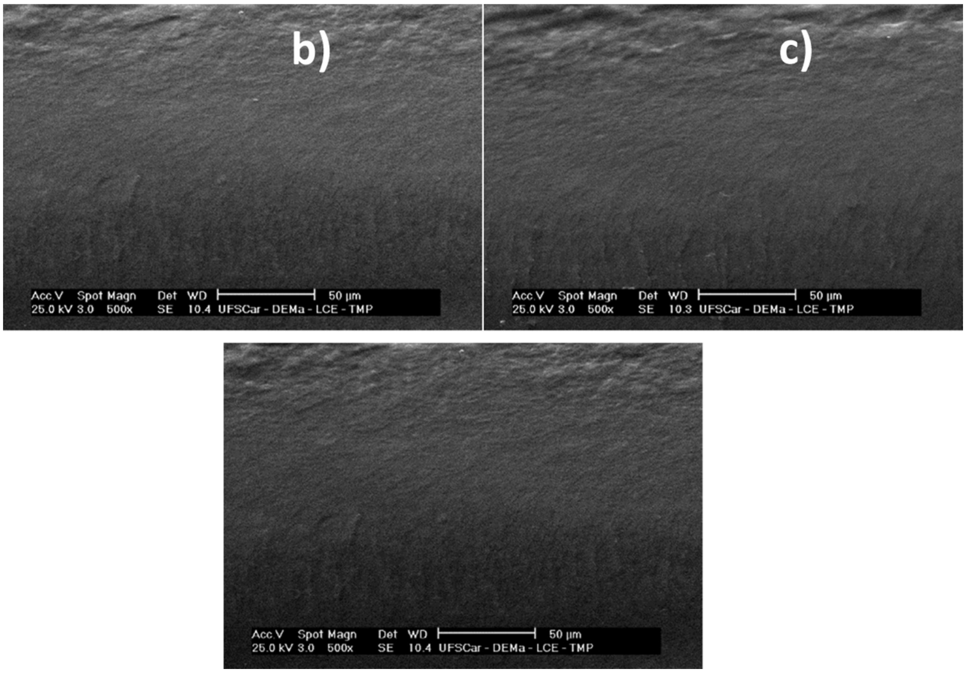

Fig. 1. SEM micrographs of the freeze-fractured surfaces of PVA-chitosan blends, (a) 90:10, (b) 75:25 and (c) 50:50.