



High performance poly (lactic acid)/bio-polyamide11 through controlled chain mobility



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ARTICLE INFO

Article history:

Received 9 April 2017

Received in revised form

26 June 2017

Accepted 2 July 2017

Available online 3 July 2017

Keywords:

Poly (lactic acid)

Polyamide11

Polyethylene oxide (PEO)

Blending

Toughening

ABSTRACT

This study shows that controlled PLA chain mobility in poly (lactic acid)/polyamide11 (PLA/PA11) blends can lead to high performance materials. The addition of an appropriate amount of polyethylene oxide (PEO) or polyethylene glycol (PEG) to a PLA/PA11 blend reduces the interfacial tension and increases the interfacial interactions due to an increase in the PLA chain mobility. The mechanical properties of (PLA-PEO)/PA11 50/50 systems are highly dependent on the PEO composition and at an optimal PEO concentration show a remarkable improvement in the Izod impact strength with specimens demonstrating 17.5 times the impact strength of the neat PLA and 3 times that of neat PA11. Also, these same blends show exceptional ductility with an elongation at break of 275% as compared to 5% for the neat PLA and 6% for PLA/PA11 without added PEO. Analysis of the fracture surface of the tough blends after impact indicates controlled interfacial debonding/cavitation at the continuous PLA/PA11 interface which leads to extensive shear yielding in the surrounding matrices. An excellent correlation is found between the optimal PEO composition for high performance properties and PEO limited miscibility in the PLA phase. When PEO phase separates in the PLA it tends towards the PLA/PA11 interface and provides a locus of failure for interfacial debonding. PEG is not as effective as PEO and it has virtually no effect on the mechanical properties of the PLA/PA11 blend since it phase separates at lower concentrations, thus limiting its effect on PLA mobility and ultimately providing insufficient plastic deformation to the PLA matrix. These results indicate that controlled PLA chain mobility through the use of an optimal concentration of an appropriate plasticizer is a highly effective approach towards the development of high performance PLA/PA11 blends.

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1. Introduction

The development of high performance biomaterials has made important inroads as a replacement of commodity polymers in recent years [1,2]. Poly (lactic acid) (PLA) is a biobased polymer and has significant potential due to its high tensile strength and modulus [1,3]. However, PLA suffers from inherent brittleness which limits its application [1,4]. Different strategies including blending, plasticization, controlled crystallization and copolymerization have been employed to compensate for its mechanical property deficiencies [1,5–11]. Blending with various bio and synthetic polymers [5–7,12–16] have been used to toughen PLA. However, finding a biobased polymer that enhances PLA mechanical properties has always been a challenge.

Polyamide11 (PA11) is a high-performance biopolymer with high elongation at break and impact strength [17]. Only a few studies have been carried out so far on PLA/PA11 blends [2,18,19]. In a previous work [20] on PLA/PA11 blends, a very fine dispersed phase size, high level of morphology stability and delayed PA11 crystallization behavior was related to significant PLA/PA11 interfacial reactions. A self-compatibilization behavior resulting from interfacial interactions in PLA/PA11 blends was reported by Stoclet et al. [18]. Although they did not observe a significant improvement in the mechanical properties of PLA/PA11 blends at room temperature, the PA11 dispersed phase provides a reinforcing effect to the rubbery PLA matrix at temperatures higher than the T_g of PLA. Thus, a reduction in the T_g of PLA, could be an approach to enhance the performance of PLA based blends with a proper level of interfacial adhesion.

A common approach to improve the flexibility of glassy polymers is the plasticization of the amorphous phase. Poly(ethylene glycol) (PEG) [21], poly(ethylene oxide) [22,23], citrate esters [24]

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and triacetone [25] are the most efficient plasticizers for PLA. Among the most interesting results, it has been shown that in most plasticized PLA systems, increasing the plasticizer concentration results in phase separation at a certain plasticizer concentration depending on the plasticizer molecular weight and chain architecture [26–28]. Pillin et al. [27] studied the miscibility of PLA and PEGs with different molecular weights. They showed that phase separation is caused by the PLA crystallization which increases for PEGs with lower molecular weight. Depletion of an excessive amount of plasticizer from the growing PLA spherulites increases stiffness and decreases the strain at break of plasticized PLA [28].

Only a few studies have rigorously investigated the effect of enhanced chain mobility and flexibility through plasticization on the morphology/mechanical properties relationship in polymer-polymer blends [3,6,29]. In a previous work from this laboratory the role of polymer chain mobility, through PA plasticization in reactive brominated poly(isobutylene-co-p-methylstyrene) BIMS/PA blends was studied [29]. The enhancement of the PA chain mobility upon addition of an optimum content of 5–10% plasticizer was found to significantly affect the extent of reaction, the overall dynamics and dispersed phase size of the BIMS/PA blend. Recently Hillmyer et al. [3] studied the effect of the addition of polyalkylene glycol liquid (PAG) plasticizer on the stress-strain behavior of reactively compatibilized PLA/polypropylene-based elastomer (PBE) blends. They used an epoxy-functionalized terpolymer (PEGMMA) as a reactive compatibilizer for the PLA/PBE blend. They demonstrated that PAG was formed as small droplets (200–400 nm) dispersed in the PLA phase and that PAG did not significantly restrict the compatibilizing ability of the PEGMMA. Their quaternary systems of PLA/PBE/PEGMMA/PAG showed an increase in the elongation at break to 110% as compared to 7% for pure PLA which was attributed to the improved interfacial adhesion and micro-void initiating effects associated with the PAG plasticizer.

The objective of this work is to examine the potential of enhanced PLA chain mobility, through addition of plasticizers, as a route to yield high performance mechanical properties in PLA/PA11 blends. This work will examine the effect of plasticizer type and concentration on the morphology/mechanical properties relationship.

2. Experimental section

2.1. Materials

PA11 (Rilsan BMNO TL) and PLA (PLA 3001D), were obtained from Arkema and Natureworks, respectively. Poly(ethylene glycol) (PEG) with a molecular weight of 4000 g/mol and Poly(ethylene oxide) (PEO) water-soluble polymer (POLYOX™ WSR-N10) with a molecular weight of 10^5 g/mol were produced by Aldrich and Dow, respectively. As is typical in the literature, it should be noted that high molecular weight polymers of ethylene oxide (EO) are generally referred as poly(ethylene) oxide (PEO), whereas polymers with molecular weights lower than 30000 g mol^{-1} are called poly(ethyleneglycol) (PEG) [30]. PEO and PEG were dried at 40°C and PLA and PA11 were dried at 70°C under vacuum for 48 h before use.

2.2. Interfacial tension

The Neumann triangle (NT) approach was used as an in situ measurement of interfacial tension of PLA-PEO and PLA-PEG with PA11 at different PEO and PEG concentrations. This method is applied on a ternary immiscible system demonstrating a partially wet morphology at equilibrium with a three phase contact line [31]. In this study PE was used as the third component to prepare a

partially wet (PLA-plasticizer)/PA11/PE ternary blend. Although the NT method gives relative values, it is possible to calculate the absolute value of interfacial tensions when the magnitude of at least one pair of the components is known [31]. The contact angle values ($\theta_{\text{PLA-plasticizer}}$, θ_{PA11} and θ_{PE}) and also the relative interfacial tensions ($\gamma(\text{PA11/PLA-plasticizer})/\gamma(\text{PA11/PE})$, $\gamma(\text{PA11/PLA-plasticizer})/\gamma(\text{PLA-plasticizer/PE})$, $\gamma(\text{PLA-plasticizer/PE})/(\gamma(\text{PA11/PE}))$) were determined for at least 20 partially wet droplets at the interface by applying the NT method on the micrographs of the (PLA-plasticizer)/PA11/PE blend morphology. The detailed procedure for the NT method is described elsewhere [31].

2.3. Blend preparation

PLA and PA11 were dried at 70°C and PEO was dried at 40°C in a vacuum oven for 48h before mixing. All samples used for the study of the effect of plasticizer on morphology and the PLA/PA11 interfacial tension were prepared in an internal batch mixer (Plasti-Corder, Brabender, with a total volume of 30 ml) with roller blades, under nitrogen atmosphere. The rotor speed was maintained at 50 rpm and the processing temperature was set at 200°C . All samples used for mechanical analysis were prepared with a Leistritz ZSE 18HP co-rotating twin screw extruder equipped with a pelletizer. A screw with a L/D ratio of 40 and a speed of 100 rpm were employed. For the ternary (PLA-PEO)/PA11 blends, first a PLA/PEO masterbatch was prepared and then this was melt blended with PA11. All the blend components were first dry mixed and subsequently added to the extruder for melt mixing. The processing temperature was controlled at the different zones of the extruder in order to obtain an ascending temperature profile from 180°C at zone 1 to 200°C at the die. After exiting the extruder, the extrudate samples were quenched in a water bath and granulated with a pelletizer. The granulated samples were dried at 80°C in a vacuum oven for 24 h before injection molding. Type I dog-bone samples (ASTM D638) and impact test specimens with dimensions of $63.5 \times 12.7 \times 3.2 \text{ mm}$ were prepared with a Sumimoto SE50S injection molding machine with an average temperature of 200°C and a screw speed of 100 rpm.

2.4. Polarized and optical microscopy (POM)

A Nikon Optiphot-2 microscope equipped with a light polarizer was used to examine the PLA spherulites of PLA/PEO blends during iso-thermal crystallization. Under the microscope, a thin film of each sample, sandwiched between two microscope slide cover glasses, was heated at a rate of $20^\circ\text{C}/\text{min}$ to 200°C in a Mettler FP-82HT hot-stage equipped with a Mettler FP-90 central processor. The samples were cooled down subsequently to the desired temperature and micrographs were taken with a CCD camera. Streampix v. III and Visilog v.6.3 software were used to analyze the micrographs.

2.5. Microtomy and scanning electron microscopy (SEM)

Prior to pelletizing the samples, 1 cm long cylinders were cut out from some strands. Blends were then cryo-microtomed using a Leica-Jung RM2065 microtome equipped with a liquid nitrogen cryo-chamber and a glass knife. PLA was extracted with chloroform and in ternary samples PEO was extracted with water. The samples were then coated with a 15 nm thick gold layer and a Field Emission scanning electron microscope SEM (JSM 7600F, JEOL) at a voltage of 5 kV was used for morphology observation.

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