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Structure, properties and interfacial interactions in poly(lactic acid)/polyurethane blends prepared by reactive processing

Balázs Imre^{a,b,*}, Dániel Bedő^{a,b}, Attila Domján^c, Peter Schön^d, G. Julius Vancso^d, Béla Pukánszky^{a,b}^aLaboratory of Plastics and Rubber Technology, Budapest University of Technology and Economics, P.O. Box 91, H-1521 Budapest, Hungary^bInstitute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary^cInstitute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary^dMaterials Science and Technology of Polymers, MESA⁺ Institute for Nanotechnology, University of Twente, Enschede NL-7500, The Netherlands

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ABSTRACT

Polyurethane elastomers are promising candidates for the impact modification of PLA producing blends for example for biomedicine. Poly(lactic acid) (PLA)/polyurethane elastomer (PU) blends were prepared by reactive processing and physical blending as comparison. The blends were characterized by a number of techniques including microscopy (scanning electron microscopy, SEM, and atomic force microscopy, AFM), rotational viscometry, thermal (dynamic mechanical analysis, DMA), and mechanical (tensile) measurements. The analysis and comparison of the structure and properties of physical and reactor blends proved the successful coupling of the phases. Coupling resulted in more advantageous structure and superior mechanical properties compared to those of physical blends as confirmed by morphology, macroscopic properties and the quantitative estimation of interfacial interactions. Structural studies and the composition dependence of properties indicated the formation of a submicron, phase-in-phase structure which positively influenced properties at large PU contents. The results strongly support that reactive processing is a convenient, cost-effective and environmentally friendly technique to obtain blends with superior properties.

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1. Introduction

The interest in using polymeric materials derived from renewable resources increases by the day because of the considerably improved environmental awareness of society and concerns about the depletion of petrochemical based plastics [1]. Poly(lactic acid), PLA, seems to be a polymer of choice which satisfies this surge of demand, the requirements of large scale processing and application, at the same time. PLA has several advantages, among others

it can be produced from renewable resources [2] thus its application does not generate supplementary CO₂ emission [3], it is recyclable and compostable, it has good stiffness and strength, and its properties can be modified and adjusted to a large number of applications in various ways [4–6]. On the other hand, this polymer has some drawbacks as well, including moisture sensitivity, fast physical ageing, poor impact resistance and relatively high price [4–6]. As a consequence, many attempts have been made to modify it by plasticization [7–13], copolymerization [14–19], blending [20,21] or by the production of particulate filled or fiber reinforced composites [11–13,22–30].

Physical ageing leading to increased stiffness and decreased deformability contribute significantly to the poor fracture resistance of PLA. Many attempts have been made

* Corresponding author at: Laboratory of Plastics and Rubber Technology, Budapest University of Technology and Economics, P.O. Box 91, H-1521 Budapest, Hungary. Tel.: +36 1 463 2967; fax: +36 1 463 3474.

E-mail address: bimre@mail.bme.hu (B. Imre).

to improve impact resistance by blending it with elastomers. Poly(ϵ -caprolactone) PCL, for example, is a biodegradable polymer with excellent deformability and impact properties, thus it appears to be very appropriate for the modification of PLA. Unfortunately, the melt blending of the two polymers results in marginal improvement of toughness at the price of a considerable decrease in stiffness and strength as a result of complete immiscibility and weak interfacial adhesion [31,32]. In order to improve compatibility and achieve a more advantageous combination of properties, several methods have been applied, e.g. the addition of block copolymers such as PCL–PLA diblock [33–35], triblock [33,36,37] and random copolymers, a PCL–PEG copolymer [38], a PEO–PPO–PEO triblock copolymer [39] or several commercial impact modifiers [40] with various successes.

Biopolymers often contain a number of reactive groups offering excellent possibility for the reactive compatibilization of their blends. The addition of a compound miscible with one blend component and reactive towards the functional groups of the other results in the in situ formation of grafted or block-copolymers acting as compatibilizers [41–43]. The method possesses considerable potential, since structure and properties can be controlled relatively easily by the proper selection of components, blend composition and processing conditions. Two or multiple step compatibilization by maleic anhydride is a good example for this approach [44–46]. However, one-step blending and compatibilization possesses several advantages, both from an economical and environmental point of view, since it enables the elimination of several processing steps. Such a process was reported by Dubois et al. [47,48] more than ten years ago. The ring-opening polymerization (ROP) of cyclic esters initiated by the hydroxyl groups of biopolymers like starch [47], dextran [48] or partially substituted cellulose acetate [49–51] is a convenient method for the preparation of block copolymers via reactive processing, although various other combinations are also possible.

The goal of this study was to prepare PLA–PU blends with improved properties compared to those of PLA. Blends were prepared by reactive processing and physical blending. The coupling of the components was achieved in the reactive blends through the isocyanate group reacting with the hydroxyl and carboxyl end-groups of PLA, which results in the formation of PLA-b-PU block copolymer acting as compatibilizer. Reactive blends (PLA-b-PU) are compared to samples with the same composition but prepared by physical blending (PLA/PU).

2. Experimental

The PLA used in the experiments was obtained from NatureWorks (USA). The selected grade (Ingeo 4032D, $M_n = 88,500$ g/mol and $M_w/M_n = 1.8$) is recommended for extrusion. The polymer (<2% D isomer) has a density of 1.24 g/cm³, while its melt flow index (MFI) is 3.9 g/10 min at 190 °C and 2.16 kg load. Poly(tetrahydrofuran) (PTHF, $M_n = 1000$ g/mol), 1,4-butanediol (BD) and 4,4'-methylenebis(phenyl isocyanate) (MDI) were obtained from Sigma–Aldrich for polyurethane synthesis. Both PLA

and PTHF were dried in a vacuum oven before further use (110 °C for 4 h and 80 °C for 4 h, respectively). Butanediol was vacuum-distilled in order to remove any traces of water, while MDI was used as received.

In the case of the two step polymerization and blending, polyurethane synthesis (150 °C, 50 rpm, 30 min) and the homogenization of PLA and PU (180 °C, 50 rpm, 12 min) were carried out in an internal mixer (Brabender W 50 EHT). The same equipment was used for the one-step method, i.e. reactive processing (180 °C, 50 rpm, 20 min). PLA was fed into the chamber first, followed by the addition of the diols (PTHF and BD) to the PLA melt and the isocyanate (MDI) was added last. Temperature and torque were recorded during homogenization. The melt was transferred to a Fontijne SRA 100 compression molding machine (190 °C, 5 min) to produce 1 mm thick plates used for further testing.

Molecular weight was determined with size-exclusion chromatography (SEC). Chromatograms were recorded in dimethylformamide at a flow rate of 0.5 ml/min at 35 °C with a Waters chromatograph (Waters e2695 Separation Module) equipped with four gel columns (4.6 × 300 mm, 5 μ m Styragel columns: HR 0.5, 1, 2 and 4) and a Waters 2414 refractive index detector. SEC was calibrated with polystyrene standards. The results were evaluated by the Empower 2 (Waters 2008) software.

The chemical structure of the reactor blends was characterized by selective dissolution and analysis. PLA was selectively extracted from the blends with dichloromethane. 2 g sample was extracted in 160 ml solvent for 48 h. The extracted samples were dried in vacuum for 24 h. The chemical structure and composition of the separated fractions were determined by solution state nuclear magnetic resonance spectroscopy (NMR). NMR spectra were obtained by a Varian Unity INOVA spectrometer operating at the ¹H frequency of 600 MHz with 5 mm inverse detection probe, while a Varian Unity INOVA spectrometer operating at the ¹H frequency of 400 MHz with a Z-gradient 5 mm inverse detection probe was used for ¹H diffusion-ordered spectroscopy (DOSY). The ¹H-DOSY experiments were carried out using a Performa I gradient amplifier with a 20 Gauss/cm maximum gradient capability. The bipolar pulse-pair stimulated-echo (Dbppste) pulse sequence was used for acquiring diffusion data with 20 ms diffusion delay, 25 squared increments for gradient levels and 32 transients with a delay time of 16 s. The Varian DOSY package was used for the processing of the results. PLA and PU rich phases were dissolved in deuterated chloroform and dimethyl sulfoxide, respectively. The signals of the solvent were used as reference for chemical shifts. For the one-dimensional ¹H spectra 16 s delay time and 4 s acquisition time were used to get accurate integrals. Two-dimensional ¹H–¹³C correlation spectra were recorded for assignment and to map the connections in a molecule. Homonuclear single-quantum correlation (HSQC) and heteronuclear multiple-quantum correlation (HMQC) measurements were carried out under standard conditions with 2 s delay time to identify directly bonded C–H pairs and longer connections (2–3 bonds), respectively. The temperature of the measurements was 25 °C.

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