



Ductility of polylactide composites reinforced with poly(butylene succinate) nanofibers



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ABSTRACT

Sustainable “green nanocomposites” of polylactide (PLA) and poly(1,4-butylene succinate) (PBS) were obtained by slit die extrusion at low temperature. Dispersed PBS inclusions were sheared and longitudinally deformed with simultaneous cooling in a slot capillary and PBS nanofibers were formed. Shearing of PBS increases nonisothermal crystallization temperature by 30 °C. Tensile deformation was investigated by *in-situ* experiments in SEM chamber. Dominant deformation mechanism of PLA is crazing, however, there are dormant shear bands formed during slit die extrusion. Pre-existing shear bands are inactive in tensile deformation but contribute to ductility by blocking, initiating and diffusing typical craze growth. PBS nanofibers are spanning PLA craze surfaces and bridging craze gaps when PLA nanofibrils broke at large strain. Straight crazes become undulated because either dormant or new shear bands become activated between crazes. Due to interaction of crazes and shear bands the ductility increases while high strength and stiffness are retained.

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1. Introduction

During the past decade polymers produced from renewable resources were the subject of an increasing interest. Among them, polylactide (PLA) having high strength and high elastic modulus appears as the most promising candidate for the substitution of petrochemical polymers, in the various markets, mainly as packaging [1], textile [2], automobile industry [3], etc. Moreover, owing to its non-toxicity, biodegradability and biocompatibility PLA can be regarded as a promising material for biomedical application [4].

However, one main drawback of PLA is its brittle behavior at room temperature, the origin of which being attributed to the occurrence of crazing [5]. The intrinsic brittleness of PLA imposes considerable scientific challenges and limits its large-scale applications.

Overcoming this problem can be achieved by increasing the molecular mass [6], by cross-linking [7,8], by creating a branched structure and reducing the polydispersity [9,10] or by activating the dynamic response of temporary entanglements [11]. Rapid cooling also contributes to the increase of toughness by freezing larger free volume and preventing for crystallization [12].

Besides the ways that influence the deformation mechanism by changing the molecular network it is also possible to influence the

intrinsic stress distribution. For this purpose the addition of rubber fillers or toughening by voiding are used [13–21]. As a consequence, increasing the filler content, and hence, reducing the matrix ligament thickness between the filler particles, leads to the transition of deformation mechanism from crazing to shearing.

By mechanical pre-conditioning the intrinsic softening can also be obtained [22–24]. Mechanical rejuvenation by torsion or rolling of polymers inhibits localization of strain in a subsequent tensile experiment. Nevertheless due to volume relaxation, the effect of mechanical rejuvenation is only temporary.

Worth notice is the fact that the basic strategy underlying the above-mentioned approaches requires that the shear yield stress is lower than the craze stress. When this cannot be achieved then at least the craze stress should be increased as much as possible. This leads to the fact that employing such approaches causes an improvement of the ductility and toughness, but greatly reduces strength and stiffness in comparison to neat PLA homopolymer.

Unprecedented result has been reported by Lan Xie et al. in the case of nanofibrillar poly(lactic acid)/poly(butylene succinate) (PBS) composites [25]. It was shown that the formation of PBS nanofibril induced hybrid shish-kebabs crystals of PLA, conferred largely to strengthened interfacial bonding, permitted a fair combination of mild strength and modulus while the ductility increased significantly (56.4 MPa, 1702 MPa, and 92.4%) for the composites loaded with 40 wt.% PBS nanofibrils as compared to those of pure PLA. It was assumed that reinforcing phase allows the activation

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of the shear yielding mechanism in addition to crazing. As the processing method a two-stage process including intense extrusion compounding followed by slit die extrusion-hot stretching-quenching technique has been suggested [25].

In this work we propose a slit die extrusion process for modification of the PLA matrix by formation of the shear band transformation as well as the PBS nanofibers that aside from strengthening act as effective spanning PLA craze surfaces reinforcement. The solidification of PBS nanofibers is facilitated by a drastic decrease of the temperature in the dye and by acceleration of PBS crystallization by shear and elongation induced effects. All these was achieved at 3 wt.% of PBS in amorphous PLA, in contrast to 40 wt.% of PBS and crystalline PLA as used by Hsiao et al. [25]. Furthermore the present work was aimed also at studying the plastic deformation mechanisms involved during cold drawing of neat PLA and PLA/PBS composites before and after extrusion processing. For this purpose, *in-situ* tensile testing inside the SEM sample chamber were performed.

2. Experimental

2.1. Materials

PLA 4060D purchased from NatureWorks LLC (Minnetonka, MN), with density of 1.24 g cm^{-3} , weight average molar mass M_w of 120 kg mol^{-1} and polydispersity $M_w/M_n = 1.4$ as determined by size exclusion chromatography (SEC) with multi-angle laser light scattering detector in dichloromethane. D-Lactide and L-lactide contents were 18 and 82 mol%, respectively, as determined by measurements of specific optical rotation. The presence of 18% DLA prevented PLA from crystallization during thermal treatment. Poly (1,4-butylene succinate), extended with 1,6-diisocyanatohexane was a commercial product purchased from Sigma-Aldrich (USA) Co., Ltd. It shows a melting point of $120 \text{ }^\circ\text{C}$ and a melt flow index of 10 g/10 min ($190 \text{ }^\circ\text{C}/2.16 \text{ kg}$, ASTM D1238).

2.2. Sample preparation

Prior to blending, PLA and PBS were vacuum dried for 24 h at $40 \text{ }^\circ\text{C}$. Melt blends containing 3 wt.% of PBS and 0.2 wt.% of Irganox 1010 for prevention of the thermooxidative degradation and 0.2 wt.% of metal deactivator Irganox MD 1024U for additional deactivation of catalysts were prepared using a Brabender batch mixer (Duisburg, Germany) operating at $170 \text{ }^\circ\text{C}$ for 10 min at 100 rpm. Further blending was followed by extrusion of tapes using single-screw extruder (PlastiCorder PLV 151, Brabender; $D = 19.5 \text{ mm}$, $L/D = 25$, and 20 rpm) equipped with the 12 mm wide, 0.8 mm thick and 100 mm long slit die. Temperatures in the zones were 170, 150, and $135 \text{ }^\circ\text{C}$ from the feed section to the die, respectively. The slit die process parameters were as follows: temperature $-130 \text{ }^\circ\text{C}$, pressure -65.0 MPa . The extrudates were cast on a transport belt at $T = 25 \text{ }^\circ\text{C}$. The extrudates in the form of tapes approximately 0.75 mm thick and 10 mm wide were obtained. Neat PLA was also processed under the same condition to obtain a reference material. For examination of the properties of initial PLA and PLA/PBS composite 0.75 mm thick films of the materials were compression molded at $170 \text{ }^\circ\text{C}$ for 3 min, and quenched between thick metal blocks kept at room temperature.

2.3. Mechanical and thermal properties

Tensile measurements were performed according to the ISO 527-2 standard. Specimens of the gauge length of 25 mm and the width of 5 mm (ISO 527-2, type 1BA) were cut out from the compression molded films and from extruded tapes using a steel

template. For extrudates specimens oriented along the extrusion directions were prepared. Samples were tested at room temperature ($T_d = 22 \text{ }^\circ\text{C}$) using an universal testing machine Instron, Model 5582. Clip-on extensometer having the gauge length of 25 mm was used for strain measurement. The crosshead speed was constant and set to 1.25 mm/min , i.e. the initial deformation rate was 5%/min. DMTA measurements were carried out on rectangular specimens, $24 \text{ mm} \times 10 \text{ mm}$, cut out from 0.75 mm thick films, in a tensile mode using a DMTA DMA Q 800 TA Instruments (USA) apparatus at the frequency of 1 Hz and at the heating rate of $2 \text{ }^\circ\text{C min}^{-1}$. Thermal behavior of samples was probed with DSC 2920 differential scanning calorimeter (TA Instruments) during heating from $-50 \text{ }^\circ\text{C}$ to $190 \text{ }^\circ\text{C}$ with the rate of $10 \text{ }^\circ\text{C min}^{-1}$. Samples of the 7–8 mg mass were cut out from extruded PLA and PLA/PBS composites and crimped in standard Al pans. The DSC cell was purged with dry nitrogen during the measurements (20 ml/min).

2.4. Scanning Electronic Microscopy (SEM)

SEM was employed to observe the PLA/PBS composite's phase morphology. Cryogenic fracture and selective etching were applied to reveal the inner structure. For the cryogenic fracture, the composite sheets were placed in liquid nitrogen for 0.5 h, finally the samples were cryogenically fractured along the extrusion direction. The surfaces exposed by fracture were observed in SEM after sputtering with carbon, or were further subjected to selective etching of PLA. PLA was etched by a water–methanol (1:2 by volume) solution containing 0.025 mol/L of sodium hydroxide for 14 h at $15 \text{ }^\circ\text{C}$, i.e. followed the procedure described in Ref. [25]. All etched surfaces were further cleaned by using distilled water and ultrasonication prior to SEM observation. Samples were coated with a fine gold layer or carbon layer (for *in-situ* SEM observation) by ion sputtering (JEOL JFC-1200) and then examined with the JEOL JSM-5500 LV scanning electron microscope. All microscopic observations were made in the high-vacuum mode and at the accelerating voltage of 10 kV. The specimen for *in-situ* SEM observation were prepared according to the ASTM standard D638. Oar-shaped specimens, with the gauge length of 9.53 mm and the width of 3.18 mm, were cut out from the compression molded films and from extruded tapes using a steel template. *In-situ* observations of tensile experiments were conducted in a JEOL JSM-5500 LV scanning electron microscope with a Gatan MT200 microtest tensile stage with maximum load capacity of 200 N at room temperature using an accelerating voltage of 15 kV. The deformation rate of the microtest was 0.2 mm/min . During tensile process, at some strain points, the tensile process was paused and the load was held, and then SEM images were taken. It should be pointed out that a slight stress relaxation occurred during the pauses. After SEM images were taken, the tensile process was continued.

2.5. Two-Dimensional Wide-Angle X-ray Diffraction (2D-WAXD)

2-D WAXS images were registered with flat X-ray camera equipped with imaging plates (Fuji) and coupled to Cu $K\alpha$ source (sealed tube operating at 30 kV and 50 mA, Philips). In addition the X-ray measurements were performed with a diffractometer attached to Philips sealed tube X-ray source set in the reflection mode. The samples in the form of an extruded tapes were oriented along or perpendicular to the machine direction.

2.6. Rheo-optical measurements. Shear-induced crystallization test

Shear-induced crystallization of the PBS films was carried out in the Linkam optical shearing system CSS450 (Waterfield, UK). The system consists of a polarizing light microscope and a cell

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