Influence of High-Speed Extrusion on Structure and Properties of Bioplastics Blends

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Abstract

This work describes a novel, high-speed twin-screw extrusion process applied to blends of bioplastics. The blends were chosen for their ability to combine synergistic polymers to produce more robust bioplastics with diverse properties. The influence of interfacial reaction was also studied, both from the perspective of morphology development and final properties improvements. Immiscible PLA/PA11 blends were successfully compatibilized by in-situ reactive twin-screw extrusion. During processing, the molecular weight of PLA sharply decreased due to chain scission. Mechanical property improvement was realized through processing parameter optimization and addition of a chain extender.

Introduction

Blending two dissimilar polymers has long been used as a simple method to extend usage windows. Since many commercial bioplastics have limitations in properties, a logical solution is to blend resins to accomplish required specifications. Poly(lactic acid) (PLA) is a well-known bio-based and biodegradable thermoplastic polyester produced industrially from corn and sugar beets, which is becoming cost-competitive with standard packaging plastics. However, PLA has limited thermal and mechanical properties compared to other common plastics widely used in industry. Polyamide (PA) polymers can be derived from both petroleum and bio-based resources. PAs have high thermal stability and mechanical properties, but are generally more expensive than polyesters. PA11 has been produced commercially from castor oil extracts, but other bio-based polyamides, such as PA7 and dimer fatty acid polyamide (DAPA), are becoming available as well.

Many techniques have been sought for augmenting the properties of PLA, but potential issues with toxicity of additives and additional processing steps limit the viability of these options. Melt blending is a simple and widely used processing technique to manipulate the properties of plastics in one step. Most polymer blends are immiscible due to high molecular weight, poor interfacial adhesion and unfavorable interactions between polymer components. This leads to a phase separated morphology and physical properties that depend not only on the two components but the morphology and interfacial characteristics as well. The composition of the blend and rheological and interfacial properties strongly affect final shape and size of the dispersed phase. The balance between droplet breakup and coalescence phenomena is dictated by the shear processing, mixer residence time, and the viscosity and concentration of the two phases.

The present work utilizes a Technovel ultra-high speed twin screw extruder, which is unique in that it is capable of rotating at speeds up to 4500 RPM, about five times faster than conventional equipment. The extruder is purported to be suitable for nanocomposites and reactive compounding due to its high shear rate. This high mechanical energy input is expected to have the effect of better dispersion and distribution in multi-component blends and lower energy consumption compared to conventional twin screw extruders. Our previous work investigated the efficacy of transesterification reactions induced by catalyst addition during melt processing. Herein, we investigate high speed reactive extrusion of bio-based polyester-polyamide blends that have been shown to form copolymers at the interface between the phases. A chain extending stabilizer is investigated for its ability to mitigate depolymerization during high shear processing.

Materials

Poly(lactic acid) (PLA) used in this study had a specific gravity of 1.24 g/cm³, melt flow rate (MFR) of 22 g/10min (210 °C, 2.16 kg), glass transition temperature (T_g) of 60 °C and melting temperature (T_m) of 166 °C and was produced by NatureWorks LLC (Ingeo™Biopolymer 3001D, USA). Bio-based Polyamide 11 (PA 11) was supplied by Arkema (Rilsan® BESNO P40 TL, USA) and had a specific gravity of 1.05 g/cm³, MFR of 3.72 g/10min (235 °C, 2.16 kg), T_g of 45 °C and T_m of 180 °C. p-Toluene sulfonic acid (TsOH, monohydrate, ≥ 98.5%), anhydrous ethanol (≥ 99.5%), chloroform and Tris(nonylphenyl) phosphite (TNPP) were used as purchased from Sigma-Aldrich, USA.

Methods

PLA and PA11 pellets were ground into powders using a laboratory mill (Thomas Wiley® Mill, USA) with a 3 mm sieve prior to dry blending in order to provide uniform feeding and fast melting feedstock to the twin-screw extruder. They were then dry-blended to produce 50:50 weight fraction blends using a high intensity blade mixer (Prodesx Henschel Mixer, USA). Mixed 50:50 PLA:PA11 powder was dried over desiccant at 90 °C for 24 hr using a laboratory drier (RH30, Dri-air industries, USA). The twin-
screw compounding extruder (KZW15TW-45/60MG-NH-3000, Technovel Co., Japan) has a 15 mm screw diameter (60:1 L/D) with two contrasting screw configurations as shown in Figure 1: (a) early mixing stage (SP3), and (b) late mixing stage (SP3-1). The processing temperature was set to 205 °C in all zones except the feed zone, which was at 190 °C. Vacuum was applied (28 in. Hg) to the vent port just before the die to remove residues and water produced from the condensation reaction. TsOH catalyst solution (0.01 g/ml) in anhydrous ethanol was fed using a peristaltic pump (ISM404B, Ismatec SA, Switzerland) at a flow rate of 2.7 µl to introduce 0.5 wt% catalyst, and TNPP stabilizer solution (0.08 g/ml) in anhydrous ethanol was fed using a second peristaltic pump (Masterflex L/S, Cole-Parmer, USA) at a flow rate of 3.2 ml/min to introduce 4 wt% stabilizer on a basis of PLA/PA11 powder feed rate (7.2 g/min) before entering the transition zone of extruder. Optimal catalyst and stabilizer loading levels were determined in a previous study. Extrusion was performed at 250, 500, 1000 and 2000 rpm. The blend resin was extruded through a strand die, cooled in a water bath, and then pelletized.

Sample Preparation

For mechanical and rheology properties testing, the extruded pellets were dried at 90 °C in a vacuum oven for 12 hours and then molded into tensile test bars (13 × 3 × 2 mm) and disks (25 mm diameter) using a micro-injection molder (Daca instruments, USA) at 205 °C for 5 min for PLA/PA11 blends. All tensile bars were annealed at 100 °C for 3 hours to achieve uniform crystallinity.

Characterization

The PLA molecular weight was determined using an intrinsic viscosity method. Samples were dissolved in chloroform and filtered through hydrophobic filter membranes to eliminate contamination and PA11 fraction. Filtered PLA solution was dried and then redissolved in chloroform to achieve 15 mg/ml solutions. The sample solution was tested with an Ubbelohde viscometer in a constant temperature water bath at 30 °C. The result of efflux time for solution was as by $\eta_s$ and $\eta_r$ versus concentration, C, and the intrinsic viscosity, $[\eta]$, was obtained from the intersection of the two plots extrapolated to zero concentration. Here, $\eta_s$ and $\eta_r$ are the specific and relative viscosity, respectively. The average molecular weight, M, was calculated following the Mark-Houwink and Sakurada equation below.

$$[\eta] = KM^{a}$$  \hspace{1cm} (14)

Where K and a are Mark-Houwink constants, reported as 0.0131 mL/g and 0.777 respectively for the chloroform solvent.

The state of dispersion of the PLA/PA11 blend was observed by field emission scanning electron microscopy (FE-SEM) (JSM-7401F, Jeol Co., Japan). Pellets or strands of the blend samples as-extruded were cryofractured under liquid nitrogen, and the fracture surfaces were coated with thin layers of gold to aid in imaging. To improve the contrast in the fractured surfaces, the specimens were treated in 0.1 M sodium hydroxide (NaOH) solution for 21 hr to etch out the PLA phase and then dried another 24 hr. Then, Image-Pro Plus (v.6.0) software was used to count and measure the droplet sizes from at least five independent SEM images between 300 and 1000 droplets per sample.

The mechanical properties of microinjection molded bars were tested at room temperature using an Instron machine (Model 4444) in accordance with ASTM D638. The tests were conducted at a crosshead speed of 50 mm/min with the strain rate ($\dot{e}$) calculated as 3.8/min. At least five samples of each composition were tested.

Results and Discussion

The first task was to quantify the extent of degradation that the rigorous mixing conditions caused in the PLA. Intrinsic viscosity measurements are highly sensitive to concentration and impurities, but when error estimation gis included they can indicate relative trends in molecular weight. As shown in Figure 2, after extrusion at low screw speed the PLA molecular weight actually increased, likely due to well-dried resin and devolatilization that yielded condensation reactions at chain ends. However, when catalyst was added the molecular weight dropped precipitously. It should be noted here that only the SP3-1 screw profile was used for TNPP chain extension experiments and PLA-TsOH homopolymer experiments. It appears that the damage sustained by the polymer was much greater when PA11 was not present. This could be due to lower catalyst concentration in PLA (presuming some was in the PA11 phase), or to lower PLA specific energy exposure when PA11 was present (less PLA mass...
for same energy input). However, the molecular weight drop relative to uncatalyzed samples occurred in both pure PLA extrusions and blend extrusions. Finally, TNPP did have the effect of slightly improving molecular weight in both pure PLA and blend processes.

Figure 2. Molecular weight of PLA with addition of TsOH or both TsOH and TNPP stabilizer in the two screw configurations for the pure PLA and PLA/PA11 blends.

Figure 3 shows example SEM images that were used to analyze the droplet size distribution under various processing conditions. For all blends, PLA formed the matrix phase and PA11 formed spherical droplets within the matrix. It is clear that overall larger droplets were observed when catalyst was added. This is likely due to lower molecular weight of the PLA and thus reduced viscosity.

Figure 3. Droplet size comparison for (a) uncatalyzed and (b) a (d) catalyzed PLA/PA11 50/50 blends extruded at 250 rpm.

Droplet size histograms that quantify the morphology at various processing conditions are provided in Figure 4. Comparing all the diagrams, it is clear that increasing the screw speed has the effect of broadening the size distribution. This broadening influence is least significant for uncatalyzed SP3-1 blends, where droplet sizes remain below 4 mm on average, and the TNPP stabilized blends, where a broad distribution is observed regardless of screw speed. The lack of dependence on screw speed indicates that droplet coalescence occurs and that even in the presence of catalyst the droplet interface is not stabilized enough to prevent coalescence. Although only one result is shown for the early mixing zone screw (SP3), this indicates that morphology is not significantly affected by the location of the mixing zone in this case.

Figure 4. Droplet diameter variation as a function of screw speeds for different screw configurations: PLA/PA11, PLA/PA11/TsOH and PLA/PA11/TsOH/TNPP blends for 50/50 weight fraction.

Tensile testing results of representative specimens and average energy at break results are shown in Figure 5. Upon observation it is clear that addition of catalyst had a significant effect on bulk mechanical properties, even though little change was observed in morphology. However the broader droplet size distribution is reflected in the larger error bars for repeat tests. Also, a downward trend in mechanical properties was observed when increasing the screw speed. The TNPP stabilizer did not appear to positively influence the mechanical properties, though a consistently higher maximum tensile stress was observed.

Figure 5. Tensile testing results for extruded PLA/PA11 blends processed with the SP3-1 screw (left) stress-strain curves for blends extruded at 250 rpm (right) Average energy at break from five tensile samples at different screw speeds.
Conclusions

The effects of interfacial reaction, stabilization and extruder screw profile were investigated for a biobased polymer blend. Molecular weight analysis, morphology and mechanical property testing were used to verify and track the effects of the reactive processing. The mechanical properties were improved, showing increasing strain at break, max tensile stress and energy at break, while PLA matrix degradation caused a decrease in Young’s modulus and tensile strength.

Increased PLA molecular weight was observed at lower screw speeds (250 rpm), but this effect was overcome by extreme mechanical stress at the highest screw speeds and when catalyst was added. To overcome the degradation from addition of TsOH catalyst, TNPP stabilizer was introduced to retain PLA molecular weight, and molecular weight recovery was observed compared to catalyzed blends. It can be concluded that screw design should be carefully considered to optimize the mixing and exchange reactions, especially if extreme shear rates are to be effective for mixing operations. In addition, more specific transesterification catalysts are required that do not cause simultaneous chain scission. This one-pot reactive extrusion process holds promise for other immiscible blends to achieve enhanced compatibility and properties.

References