Mechanical and Thermal Properties of PLA/PBS Co-continuous Blends Adding Nucleating Agent

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Abstract

The influence of nucleating agents (nano-sized calcium carbonate and sodium benzoate) on mechanical and thermal properties of PLA/PBS co-continuous blends was investigated. PLA/PBS 60/40, 50/50, 40/60 wt% blends were compounded with NPCC or SB (0.5 and 1.0 phr) in a twin-screw extruder and fabricated into thin sheets by hot pressing. DSC was used to study glass transition temperature ($T_g$) and percentage of crystallinity ($\%X_c$) of the blends. Morphology of fractured surface was examined using SEM. It is found that the PLA/PBS 50/50 wt% blend was co-continuous structure even incorporating NPCC or SB of 0.5 and 1.0 phr. Adding SB of 1.0 phr caused the PLA dispersed phases in the PLA/PBS 40/60 wt% to be smaller droplets distributed in the continuous PBS matrix. On the other hand, adding NPCC of 1.0 phr into PLA/PBS 60/40 wt% produced elongated continuous phase of PBS stripped out of PLA matrix. Adding SB into PLA reduced $T_g$ from 63 to 60 °C, while NPCC nucleated higher $\%X_c$ of PLA phases in all blends. Tensile strength, elongation at break and energy at break of the blends were reduced when filled with NPCC and SB. This is due to increasing in crystallinity of the PLA phases and the presence of stress concentrators in the blends.

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1. Introduction

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The blending of conventional polymers has been extensively employed to develop new polymeric materials. However, because of unfavorable enthalpy of mixing for two polymers, most polymer blends are immiscible and thus form phase-separated morphology: disperse domain structure in the matrix phase and co-continuous structure [1]. Such immiscible blends exhibit different types of heterogeneous morphology, which depend on the blend composition, interfacial tension, processing condition and rheological properties of the component.

When one component is present in the blend at a low concentration, a dispersed phase-matrix morphology is found, for which the shape of the dispersed particles can be spherical or fibrillar. As the concentration of the minor phase increases, particles become close enough and start to coalesce, reaching a point that corresponds to the percolation threshold point. Above this concentration, a greater and greater proportion of the minor component is incorporated into the percolation structure until at a certain volume fraction all the material of the blend components becomes part of a single percolating structure. This morphological structure is called dual-phase continuity or co-continuity, with each phase remaining continuously connected throughout the bulk of the blend. Co-continuous structures can be regarded as the coexistence of at least two continuous structures within the same volume. Blends with co-continuous structures may combine the properties of both components in a favorable way, for example, mechanical moduli [2].

Panyad and Hongsriphan [3] reported that when PLA content was up to 40 wt% in PBS/PLA blend, PLA dispersed phases were elongated and presented in uneven shapes. This resulted from the combination of low interfacial interaction between PLA and PBS and much higher viscosity of the PLA dispersed phases. When the PLA content was up to 50 wt%, the co-continuous morphology in polymer blend was formed. This co-continuous blend provided the highest tensile strength and elongation at break even though there was no compatibilizer modified the interfacial adhesion between phases.

Poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) are known as biodegradable polyesters with good mechanical properties and degradability. Especially, PLA has been widely used in biomaterial applications because of its good biocompatibility and various physical properties. But its brittleness is a major defect for many applications, thus, studies on PLA blends with other polymers were carried out in order to modify various properties [4]. Bhatia et al. [5] blended PLA with PBS and reported that the blend was partial miscibility with the PLA/PBS blend of up to 80/20 wt% composition. PBS reduced the brittleness of PLA, thus making it a contender to replace plastics for packaging applications. However, tensile strength, modulus and percentage (%) elongation at break of the blends decreased with PBS content. Lui et al. [6] blended PLA with poly (ethylene/butylene succinate) (Bionolle) and found that adding Bionolle aided in crystallization of PLA. Bionolle concentration led to a slight increase in the strain-at-break of the blends but a decrease in the Young's modulus and ultimate tensile strength. Yokohara and Yamaguchi [7] studied the structure and properties of binary blends composed of poly(lactic acid) (PLA) and fibrous poly(butylene succinate) (PBS) and compared with those of blends having spherical particles of PBS in a continuous PLA phase. PBS particle, which showed nucleating ability for PLA, led to a high degree of crystallinity and enhanced the cold crystallization in the heat process.

In general, it is known that nucleating agents enhance the nuclei generation of semi-crystalline polymers in crystallization process and leads to the higher crystallization rate at higher temperature, resulting in increasing crystallinity. Thus, the utilization of nucleating agents improves physical and mechanical properties, processability, and productivity in mold processing [8]. Recently, nano-sized calcium carbonate (CaCO₃ or NPCC) has received a lot of attention because of its wide range of potential applications and its low cost. Various methods, such as high gravity reactive precipitation, have been developed to prepare NPCC particles with a narrow size distribution. Kim et al. [9] studied the effect of the CaCO₃ particles on the thermal stability of the PLA-based. They found that the tensile strength and modulus value of the composite were improved greatly without a significant loss in the elongation at break when the NPCC was incorporates up to 30 wt%. Sodium benzoate (SB) with fine particle sizes is
one of the interesting candidates for using as nucleating agents, because it meets several requirements as a nucleating agent in that it possesses a polar group, is insoluble in a polymer, and is crystallized on cooling before the polymer. There has not been a report on effect of sodium benzoate as a nucleating agent in biodegradable polymers. Therefore, JANG et al. [10] studied the effect of sodium benzoate as a nucleating agent on polypropylene. They found the addition of the nucleating agent up to its saturation concentration increased the crystallization temperature by 15°C, and was concluded that the sodium benzoate acted as a good nucleating agent for α-form PP.

In this study, we focus on the influence of nucleating agents, namely NPCC and SB, on mechanical and thermal properties of PLA/PBS co-continuous blend. Such a blend would benefit to film or sheet application since they provide high tensile strength and high elongation at break. The blends were compounded with nucleating agents in a twin-screw extruder and fabricated into thin sheets by hot pressing. Differential scanning calorimetry (DSC) was used to study the crystallinity of the blends, and morphology of fractured surface was examined with scanning electron microscope (SEM). Mechanical properties of the blends were determined by means of tensile test.

2. Experimental Procedure

2.1. Materials

Polymers used in this study were poly(lactic acid) (PLA), (Ingeo™2003D, NatureWork LLC, USA) with MFI of 6 g/10 min (210°C, 2.16 kg.), and poly(butylene succinate) (PBS) (GS Pla®FZ91PD, Mitsubishi Chemicals, Japan) with MFI of 6 g/10 min (190°C, 21.18 N). Sodium benzoate (SB, 99.6% purity) was purchased from Ajax Finechem Pty Ltd. and used as received. Nano-sized precipitated calcium carbonate (NPCC201) was supplied by Behn Meyer Chemical (Thailand). It was coated with stearic acid for good dispersion.

2.2. Compounding and Fabrication

Blends of PLA, PBS, and nucleating agents (NPCC or SB) were compounded by melt mixing in a twin-screw extruder (SHJ-25, Yongteng, China) with a screw speed of 60 rpm and temperature profile ranging from 135°C to 155°C. A set of PLA/PBS blend was prepared as following weight ratio: 40/60, 50/50 and 60/40 wt%. Nucleating agents (NPCC or SB) of 0.5 and 1.0 phr were added into polymer blends in separate sets of blending.

Before compounding, PLA and PBS pellets were dried at 50°C in an air-circulating oven for 24 hrs, and NPCC and SB were dried at 110°C for 24 hrs in order to minimize moisture. The mixture of PLA, PBS and NPCC or SB were manually premixed by tumbling in plastic box, and subsequently fed into the extruder for melt compounding. The extrudate was cooled in a water bath and subsequently granulated by pelletizer.

Compressed sheet with a thickness of 0.25 mm were prepared using a hot press (Labtech, Thailand) at 170°C, pressing pressure of 120 bar and pressing time of 3 min. Then, compressed sheet were dried in oven at 50°C for 24 hrs and stored in desiccator prior to further testing.

2.3. Characterization and Testing

Tensile properties of compressed samples were studied in accordance to ASTM-D882 using a Universal Testing Machine (Instron, Model 5969, Instron Engineering Corporation, USA). The test specimens of neat PLA, neat PBS, PLA/PBS blends, and PBS/PLA blends adding nucleating agents were conditioned at room temperature for 24 h prior to testing. The test was performed with a crosshead speed of 50 mm/min at room temperature and the average of seven measurements was reported.
Morphology of the blends was examined by a scanning electron microscope (SEM) (Jeol, JSM 5410LV). Specimens were tensile fracture. The fractured surface was gold coated prior to inspection to avoid electrostatic charging.

Thermal analysis of neat PLA, neat PBS, PBS/PLA blends, and PBS/PLA blends adding nucleating agents were determined under a nitrogen atmosphere by using a differential scanning calorimeter (DSC, Perkins-Elmer). The sample weight used was approximately 3-5 mg weight. The samples were tested in a heat-cool-heat mode, with the heating rate and the cooling rate of 10 °C/min. Temperature scan was performed from 30 °C to 200 °C for neat PLA and PLA/PBS blends. For neat PBS was heated from 30°C to 150°C at the same rate. The DSC crystallinity (%X_c) was calculated by using following equation:

\[ \% X_c = \frac{(\Delta H_m - \Delta H_f)}{\Delta H_f^0} \times 100\% \]  (1)

where \( \Delta H_m \) is the observed enthalpy of fusion obtained from the 2nd heating process of DSC measurement, \( \Delta H_c \) is the enthalpy of crystallization, \( \Delta H_f^0 \) is the enthalpy of fusion of the completely crystalline materials at the equilibrium melting temperature, and \( w \) is the PLA or PBS weight ratio in polymer blend. Here, \( \Delta H_f^0 \) is 93 J/g and 110.3 J/g for PLA [16] and PBS [3], respectively.

3. Results and Discussion

3.1. Morphology of neat PLA, neat PBS, PLA/PBS blend, and PLA/PBS blends adding NPCC or SB

Fig.1 shows SEM micrographs of cryo-fractured surface of neat PLA, neat PBS, PLA/PBS blend, and PLA/PBS blends adding 1.0 phr of NPCC and SB. Under 500X magnification, smoother fracture surface of neat PLA indicates brittleness of polymer matrix. Meanwhile, neat PBS was fractured showing rougher surface than neat PLA revealing ductile behaviour. With PLA/PBS 50/50 wt% blend (PLA50), the co-continuous morphology was formed and cryo-fracture failure in ductile behavior was evident [3, 5, 12]. In 40 wt% PLA in PLA/PBS blend (PLA40), the phase inversion was present showing droplets of PLA dispersed phases. This is attributed to the combination of low interfacial adhesion between PLA and PBS phases, and much higher viscosity of the PLA dispersed phases in relatively lower viscosity PBS matrix. In contrast, dispersed phases of PBS in 60 wt% PLA blends (PLA60) could not be seen clearly.

In Fig.A-2, agglomerates of NPCC in PLA matrix were observed and the crack propagation groove was directly generated from the agglomeration. On the other hand, cryo-fractured surface of PBS adding NPCC of 1.0 phr was rougher implying local ductile were generated during the fracture. Adding NPCC or SB into PLA50 did not change the co-continuous morphology, although some spherical dispersed phases were observed indicating slightly change in melt rheology of the blends.

For PLA40, it is found that PLA dispersed phases were smaller compared to non-filled blend. This is due to higher shearing stress introducing by the relatively higher viscosity of PBS matrix mixing with NPCC. Likewise, fracture surface of PLA60 adding NPCC of 1.0 phr showed elongated continuous phase of PBS which were stripped from PLA matrix.

In PLA adding SB, it is seen that there are less crack propagation lines on the fracture surface and the crack grooves are more emphasized. This indicates more brittleness of filled polymer as confirmed by tensile tests which is discussed later. Interestingly, with the addition of SB in PLA40, the PLA dispersed phases became small droplets distributed in the continuous PBS matrix [1]. However, morphology of PLA60 adding SB presents co-continuous phases similarly to the PLA50.
3.2. Tensile properties of neat PLA, neat PBS, PLA/PBS blend, and PLA/PBS blends adding NPCC or SB

Tensile strength, elongation at break, and energy at break of neat PLA, neat PBS, and PLA/PBS blends adding 0, 0.5 and 1.0 phr of NPCC or SB are presented in Fig.2. It is clear that tensile strength of neat PLA is somewhat higher than neat PBS. Adding NPCC and SB into neat PLA reduce its tensile strength, elongation at break, and energy at break due to the presence of stress concentration. Agglomeration of NPCC is clearly evident in SEM micrograph which they acted as stress concentrators for crack initiation and thus reduced the energy at break. Meanwhile, the adding of SB into PLA caused the polymer matrix to be very brittle. The specimen of PLA adding 1.0 phr SB could not be pulled out from the hot pressing mold since they were broken down during the peel-out.

For neat PBS, it is found that adding NPCC of 1.0 phr increased elongation at break and thus improved energy at break of the specimen. This is due to well-dispersed NPCCs acted as internal lubricant in the PBS matrix since they were pre-treated with steric acids. In contrast, agglomeration of SB became stress concentrators in the ductile PBS reducing the tensile strength, elongation at break, and energy at break.

For PLA/PBS blends, the co-continuous structure in all ratios show the same range of elongation at break but different value of tensile strength. PLA40 blend had the tensile strength closed to neat PBS indicating poor interfacial adhesion between phases, although they are partial miscible as discussed later in DSC results. Increasing PLA content up to 60 wt% increased tensile strength of the blends due to the stiffness of the PLA strips wrapping along with PBS continuous phases resulting that PLA60 had higher energy at break than neat PLA.

Adding NPCC of either 0.5 or 1.0 phr into the blends reduced elongation at break and energy at break. This implies that NPCC became stress concentration in the co-continuous structure. Also, NPCC increased the %Xc in PLA phases causing the already-brittle phases be more brittle. However, increasing
of %Xc in PBS phases increased tensile strength of PLA40 adding NPCC of 1.0 phr slightly compared to non-filled ones. The PLA/PBS 60/40 wt% blend with NPCC of 1.0 phr gave the highest.

For SB, it is seen that adding SB into the blends decreased elongation and energy at break, especially in PLA40. As seen previously in SEM, the PLA dispersed phases in PLA40 became small droplets distributed in the continuous PBS matrix. These PLA droplets themselves behave as large stress concentrators in the blend with poor interfacial adhesion between them and the PBS matrix. In PLA60, it is seen later in DSC result that SB nucleated higher crystallinity in PLA matrix producing the co-continuous phases with higher brittleness.

3.3. Thermal properties of neat PLA, neat PBS, PLA/PBS blend, and PLA/PBS blends adding NPCC or SB

The glass-transition temperature (Tg), the cold-crystallization temperature (Tcc), the melting temperature (Tm) and the percentage of crystallinity (%Xc) of neat PLA, neat PBS, and PLA/PBS blends adding 0, 0.5, and 1.0 phr of NPCC and SB are shown in Table 1. It is found that the Tg of neat PLA was 63 °C, and adding sodium benzoate (SB) into PLA reduced Tg to occur at 60 °C. In contrast, adding NPCC did not change Tg of PLA. The Tg of a polymer system can fall for a variety of reasons, including changes in tacticity, molecular weight, and retained monomer. Since SB could absorb moisture during the processing and changes into benzoic acid, it would act as a catalyst for hydrolysis of PLA molecules during the melt processing. Further study of molecular weight change of PLA adding SB is under investigated.

In addition, impact of adding SB or NPCC on cold crystallization temperature (Tcc) of PLA is clearly evident. This indicates nucleating effect of these particles during the heating process of DSC studies. It is well known that PLA molecules seldom crystallize during the cooling process due to their molecular nature. While the Tcc was decreased at lower temperature implying faster nucleating, the %Xc of filled PLA was also reduced especially in the case of adding SB. This is due to dispersion of solid particles in PLA matrix inhibited growth of PLA crystals as well as reduced crystal perfection as evident in lower Tm2.

Similarly to other reports [5,11], the blends of PLA/PBS were partial miscible as seen in lower Tg of PLA in PLA50 blend. Generally, it is found that Tg of PLA was reduced in all blends with and without NPCC or SB. Unlike filled PLA, Tcc of PLA/PBS blends adding NPCC or SB were not detected. Nevertheless, adding SB into PLA/PBS blend increase %Xc of PLA phases significantly but adding them into solely PLA did decreases %Xc of PLA. It has been reported [11] that PLA molecules would crystallize faster when there are stresses induced to orient them during the crystallization process. As such, PLA molecules in the co-continuous blend with PBS are constrained which SB in the vicinity could act as nucleating sites for them to crystallize easier.
In the case of adding NPCC, it is seen that they could nucleate higher $%X_c$ of PBS phases in all blends and reduced $%X_c$ of PLA phases slightly. Since the NPCCs are treated with stearic acid, they disperse better than SB providing relatively higher active sites for polymer molecules to nucleate. It is found that higher content of NPCC in PLA/PBS blends reduced $%X_c$ of PLA phases but increased $%X_c$ of PBS phases [13-15]. Since the $T_{cc}$ of PLA is higher than $T_{cc}$ of PBS, PBS would crystallize first during the cold crystallization process and inhibits the crystallization of PLA.
Table 1 Thermal properties of PLA/PBS blends

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*ND: No Detect

4. Conclusions

The influence of NPCC and SB on mechanical and thermal properties of PLA/PBS co-continuous blend was investigated. SEM images show that the PLA/PBS 50/50 wt% blend was co-continuous structure even incorporating NPCC or SB of 0.5 and 1.0 phr. However, morphology of PLA/PBS 60/40 and 40/60 wt% blends were modified after adding these nucleating agents because of change in melt
rheology. Tensile strength, elongation at break and energy at break of the blends were dismissing when filled with NPCC and SB. This is due to increasing in crystallinity of the PLA phases, and the presence of stress concentrators in the blends. The PLA/PBS 60/40 wt% blend with NPCC of 1.0 phr gave the highest tensile strength and the highest energy at break, however, the energy at break was 40% reduction compared to non-filled blend.

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