Poly(L-lactic) acid (PLLA) blends: Melt Flow Indexes and Tensile Properties

INTRODUCTION

Nowadays, the biodegradable polymers are gaining acceptance due to the environmental problem caused by petroleum based polymeric materials (Bitinis et al., 2011). Poly(L-lactic) acid is a biodegradable polymer which derived from renewable resources such as corn and sugar (Hashima et al., 2010; Bitinis et al., 2011). PLLA is used in various applications especially in biomedical application due to the good properties such as high tensile strength, high modulus, biodegradability, resistance and non-toxic to environment (Li and Shimizu, 2009; Alessandra et al., 2012). On the other hand, it was reported that the brittleness and low impact strength are the drawback of PLLA (Ishida et al., 2009). There are many studies investigated on the toughness improvement of PLLA, where various polymers were used for toughening agent such as rubber (Ishida et al., 2009), polyethylene (PE) (Anderson and Hillmyer, 2004), styrene-butadiene-styrene block copolymer (SEBS) (Hashima et al., 2010), poly (ε-caprolactone) (PCL) (Todo et al., 2007), and acrylonitrile-butadiene-styrene (ABS) (Li and Shimizu, 2009).

The melt blending is one of the approaches used to improve brittleness of PLLA. It was reported that PLLA blends with rubber or low molecular additives have enhanced the elongation at break (Li and Shimizu, 2009). Thus, blending between PLLA and other polymers can improve the mechanical properties especially the toughness of PLLA. However, it was reported that the mechanical properties and physical properties of polymers blends are depended on the miscibility of polymers blends (Bitinis et al., 2011).

In this study, PLLA was blended with other polymers such as acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) microsphere at 98/2 and 94/6 blend ratios. The tensile properties and melt flow index (MFI) of PLLA blends system at different blend ratios were investigated and analyzed. The result was supported with microstructure of the polymer blends.
Experimentation:

Materials:

PLLA pellets (Lacty®#5000, $M_w = 1.45 \times 10^5$, $M_n = 0.75 \times 10^5$, PD = 1.93) were supplied by Toyota Motor Co., Ltd. PLLA is a thermoplastic which derived from lactic acid. This PLLA indicates a glass transition ($T_g$) of around 60 °C, a crystallization temperature ($T_c$) of around 100 °C and a melting point ($T_m$) of around 175 °C. Acrylonitrile butadiene styrene (ABS) pellets was supplied by Toray Plastics (Malaysia) Sdn. Bhd. PLA microsphere was fabricated by using emulsion solvent evaporation method. Fig. 1 shows the microsphere of PLA microsphere taken at 350x magnification.

Fig. 1: SEM morphology of PLA microsphere at 350x magnification.

Preparation of Blend and Specimens:

PLLA and polymers consist of ABS and PLA microsphere were blended at 98/2 and 94/6 blend ratios (based on wt.%) by internal mixing machine at 180 °C and 50 rpm for 10 minutes, 5 samples have been used for each blend formulation. Next, pure PLLA and PLLA blends were compressed using hot press machine at 1500 psi and 180 °C for 2 minutes, and followed by cooling process to form sheet specimens (150 mm × 125 mm × 2 mm).

Characterization:

Tensile test was carried out by Instron-3366 universal mechanical testing machine according to ASTM-D882. Tensile test was performed at a cross-head speed of 5 mm/min. Melt Flow Index (MFI) was carried out by Dynisco Polymer Test (mode D4004) according to ASTM D1238-04 (procedure A, 190 °C/2.16 kg). The outcome of melt flow index (MFI) is the molten polymer flow through an orifice in g/10 minutes from a standard cylinder die (Ø 2.1 mm × 8.0 mm). Field emission scanning electron microscopy (FE-SEM) of the cryo-fracture surfaces was performed to characterize the morphology of pure PLLA and PLLA blends system by Leo Supra 35VP. The fracture surfaces from tensile test were immersed in liquid nitrogen (N$_2$) for 30 minutes, next samples were coated by gold sputter.

RESULT AND DISCUSSION

Tensile Stress-Strain Curves:

Figure 2 shows the tensile stress-strain curves of pure PLLA, PLLA/ABS blends and PLLA/PLA microsphere blends at 98/2 and 94/6 blend ratios. Tensile stress-strain curves of PLLA/ABS blends show the brittle fracture which indicated by low strain at break. In Fig.2 (a), tensile stress-strain curve of PLLA/PLA microsphere blend at 98/2 blend ratio shows slightly lower tensile stress and higher strain at break compared to pure PLLA (control sample) whereas tensile stress and strain at break of PLLA/ABS blend are lower than those of pure PLLA and PLLA/PLA microsphere blend. At 94/6 blend ratio, tensile stress-strain curve of PLLA/PLA microsphere blend shows higher strain at break, which is illustrated in Fig.2 (b). The tensile stress and strain at break of PLLA/PLA microsphere blend at 94/6 are higher than PLLA/PLA microsphere blend at 98/2 blend ratio.

This is might be due to the fibril structure that exists within morphology as shown in Fig.3. It is noted that the tensile stress and strain at break of PLLA/PLA microsphere blends are increased when the content of PLA microsphere is increasing. Area under stress-strain curve refers to the toughness of materials. It is found that the toughness of PLLA/PLA microsphere blend at 94/6 blend ratio is slightly higher than pure PLLA (control sample).
Fig. 2: Tensile stress strain curves of pure PLLA, PLLA/ABS blend and PLLA/PLA microsphere blend (a) at 98/2 and (b) 94/6 blend ratios.

Phase Morphology:

The microstructures of the pure PLLA, PLLA/ABS blend and PLLA/PLA microsphere blend are shown in Fig. 3. In Fig. 3 (a), tensile fracture surface is flat and smooth which indicated to the brittleness of pure PLLA. The same PLLA microstructure was reported by Vannaladsaysy et al., (2010a). Fig. 3 (b-c) exhibit to PLLA/ABS blends at 98/2 blend and 94/6 blend ratios, it is observed the ABS droplets and voids present in the microstructure which indicate to the immiscibility of the blends. These ABS droplets and voids are increased when the quantity of ABS is increased. In other words, generally PLLA/ABS system at 98/2 and 94/6 blend ratios indicate the immiscibility and macro-phase separation of two components. As known, these immiscibility and phase separation affect to physical property and mechanical property of polymers blend (Vannaladsaysy et al., 2010b). In Fig. 3 (d-e), the microstructures of PLLA/PLA microsphere blends at 98/2 and 94/6 blend ratios indicate the presence of the fibril structures. It was reported that these fibril structures and the stretched edge of fracture surface exhibit the ductility of blends (Meng et al., 2012). It is observed that there is no phase separation exists in PLLA/PLA microsphere blends.

Fig. 3: SEM morphology of tensile fracture surface of (a) pure PLLA, (b) PLLA/ABS blend and (c) PLLA/PLA microsphere blend at 98/2 blend ratio, (d) PLLA/ABS blend and (e) PLLA/PLA microsphere blend at 94/6 blend ratio (at 1,000x magnification).
**Melt Flow Index (MFI):**

Melt flow index (MFI) is a parameter which important in plastics industry, it fulfills requirement for processability which the flow properties of materials are important considered for processability (Guerreiro et al., 2012; Chui et al., 2007). MFI was calculated from the weight of molten polymers blends that flow through the orifice of standard cylinder die under the controlled temperature in 10 minutes. MFI of pure PLLA, PLLA/ABS blends and PLLA/PLA microsphere blends are shown in Fig. 4. It is observed that the MFI of PLLA/ABS blends and PLLA/PLA microsphere blends at 98/2 and 94/6 blend ratios are higher than pure PLLA. It is found that the MFI increased with the content of ABS and PLA microsphere. PLLA/PLA microsphere blends indicate the higher MFI compared those of PLLA/ABS blends. According to Liang and Ness (1997), the miscibility of polymer blends might increase the flow rate of the polymer melt. As shown in Fig. 3 (d and e), there is no obvious phase separation occurs in PLLA/PLA microsphere blends this indirectly indicate the miscibility of the blend, hence slightly increase the MFI.

![Fig. 4](image_url)

**Conclusion:**

PLLA/PLA microsphere blend at 98/2 and 94/6 blend ratios exhibit the higher strain at break and Melt flow index (MFI) compared to PLLA/ABS blends. This might be due to the miscibility of PLLA/PLA microsphere blend since no phase separation occurs in the microstructure of PLLA/PLA microsphere blend. However, PLLA/ABS blends exhibit the lower tensile stress and strain at break compared to PLLA/PLA microsphere blends due to the ABS droplets and voids are observed in the morphology which indirectly related immiscibility of PLLA/ABS blends.

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**REFERENCES**


