

Effects of reactive blending on the properties of poly(lactic acid) (PLA)/liquid polybutadiene rubber (LPB) blends

Sung-Wook Lim¹⁾, Myeon-Cheon Cho²⁾, Jae-Hoon Jeong³⁾, Ok-Bae Kim⁴⁾
and *Chang-Sik Ha⁵⁾

^{1), 2), 4)} *Korea Institute of Footwear & Leather Technology, Busan 47154, Korea*
^{1), 3), 4)} *Department of Polymer Science and Engineering, Pusan National University,*
Busan 46241, Korea
¹⁾ cscha@pnu.edu

ABSTRACT

We have conducted systematic studies to investigate the effects of reactive blending on the thermal and mechanical properties of blends of poly(lactic acid) (PLA) and a liquid rubber, polybutadiene (LPB). The toughened PLAs were prepared by melt-blending the PLA with various contents (0-9 wt.%) of the LPB in the absence or presence of dicumyl peroxide (DCP), a radical initiator. It was found that the rubber domains were homogeneously dispersed at the nanoscale in the PLA matrix up to 9 wt.% of LPB thanks to the reactive blending in the presence of DCP. Owing to the compatibilization of PLA with LPB through reactive blending, the elongation and toughness of PLA was enhanced, while the hydrolytic degradation of PLA were reduced.

1. INTRODUCTION

Poly(lactic acid) (PLA) is a compostable polymer derived from renewable sources. It belongs to the family of linear aliphatic thermoplastic polyesters commonly produced by ring-opening polymerization of lactides which are obtained from the fermentation of renewable sources such as whey, corn, potato, molasses, or sugar feed stocks. PLA possesses many attractive physical characteristics which include good clarity, high strength, biocompatibility, thermoplastic fabricability, oil resistance, and excellent barrier properties. In addition, advances in the polymerization technology have significantly reduced the production cost making PLA economically competitive with petroleum-based polymers. However, its inherent brittleness has limited its applications in many fields despite the many advantages(Choi, 2013).

In this regard, there have been many strategies to improve the toughness of PLA,

^{1), 3), 4)} Student

²⁾ Ph.D.

⁵⁾ Professor

including plasticization, copolymerization, addition of rigid fillers, and blending with a variety of flexible polymers or rubbers.

Plasticization method is used not only to improve the processability of polymers but also to enhance ductility of glassy polymers. Low molecular weight plasticizers such as diethyl bishydroxymethyl malonate, glucose monoesters, citrate esters, oligomeric lactic acid, and glycerol, which are liquid with polar groups in itself, were reported to significantly improve the ductility and impact resistance of PLA. However, they are easily migrated within the PLA matrix due to their high mobility to cause the deterioration in its long-term thermal and mechanical stability.

In this work, therefore, we performed a systematic study on the effects of reactive blending on the thermal and mechanical properties of the PLA/LPB blends with various LPB contents (0, 3, 6, 9 wt.%) by comparing the PLA/LPB blends without applying reactive blending. The reactive blending of PLA and LPB was done in the presence of DCP, as for our previous work. The chemical changes of the LPB in the PLA matrix was confirmed by the results of Fourier transform infrared (FTIR) spectra and wide-angle X-ray diffraction (WAXD) patterns. The properties of the modified PLAs were investigated through tensile testing (UTM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) micrographs. Thermal and hydrolytic degradability of PLA/LPB blends with various LPB contents were also analyzed.

2. EXPERIMENTAL WORK

2.1. Materials

PLA (grade: 4032D, L-lactic acid/D-lactic acid: 98.6/1.4 with an average molecular weight of 200,000 was purchased from Natureworks LLC. PLA was dried under vacuum at 40 °C prior to use. Liquid polybutadiene (LPB, grade: LBR-305) with molecular weight of ~260000 was provided by Kuraray Co. Ltd. Dicumyl peroxide (DCP) was purchased from Sigma-Aldrich. LPB and DCP were used as received.

2.2. Processing

All blends were prepared by batch process in Haake torque rheometer with a twin-rotary mixer (Haake Rheomix 600p, Thermo Fisher Scientific). The blending was performed at a mixing temperature of 175 °C and a rotor speed of 50 rpm with the PLA:LPB ratios of 100:0, 90:10, 80:20, 70:30, and 60:40, respectively. The blends are named "PB" for PLA/LPB melt-blends and "PBR" for PLA/LPB reactive-blends followed by two digitals indicating the weight percent of the added LPB. The PBs were prepared by blending the PLA and LPB without radical initiator for 5 minutes while the PBRs were reactively blended with 0.3 phr of DCP for additional 9 minutes after the melt-blending. The pure PLA and all blends were compressed into sheets with the thickness of 1 mm and air-cooled at a room temperature. They are used to characterize the thermal and mechanical properties as well as morphological analysis. (Lim et al. 2016)

2.3. Characterization

Attenuated total reflection-Fourier transform infrared (ATR-FTIR, Perkin Elmer) was performed by samples with potassium bromide (KBr) pellets with 32 scans per spectrum at a 2 cm^{-1} resolution. A robust single-reflection accessory (Thunderdome, Spectra-Tech Co., Ltd.) with a germanium IRE ($n=4.0$, incidence angle= 45°) was used for the ATR measurements. The film sample thickness was controlled as ca. $100\ \mu\text{m}$ by hot-pressing. Thermogravimetric analysis (TGA, TA, Q50) was carried in nitrogen atmosphere from $30\ ^\circ\text{C}$ to $800\ ^\circ\text{C}$ with a heating rate of $10\ ^\circ\text{C}/\text{min}$.) The thermal transition behaviors of samples were measured under nitrogen flow using a differential scanning calorimeter (DSC, TA instruments Q 100) at a heating rate of $10\ ^\circ\text{C}/\text{min}$. The wide-angle X-ray diffraction (WAXD) patterns of the samples were measured at room temperature in the reflection mode using an X-ray diffractometer (Rigaku, Miniflex). The CuK α radiation ($\lambda = 0.154\ \text{nm}$) source was operated at 50 kV and 40 mA, while the 2θ scan data were collected at 0.01° intervals over the range of $12\text{--}24^\circ$ and at a scan speed of $1.0^\circ (2\theta)/\text{min}$.

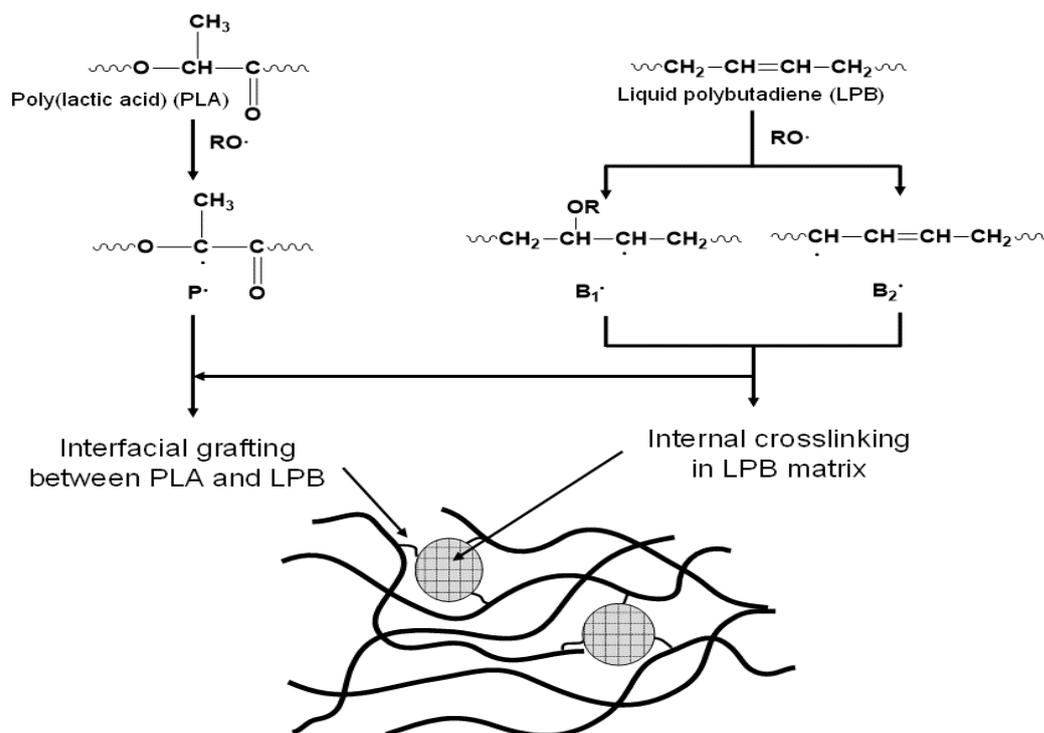
Tensile properties of the PLA and blends with a specimen dimension of $0.5 \times 5.0 \times 30.0\ \text{mm}$ (thickness \times width \times length) was measured using a universal testing machine (UTM, Korea Institute of Footwear & Leather Technology) according to the ASTM D 882-91 method. Scanning electron microscopy (SEM) was performed in the selected PLA and blends with a JEOL-6100 scanning electron microscope. The film samples were submerged in liquid nitrogen and broken. The fractured surfaces were sputtered with gold prior to the SEM examination. Thin films of the PLA and blends with the thickness of $100\ \mu\text{m}$ were prepared by hot-pressing and diced into $2.0\ \text{cm} \times 2.0\ \text{cm}$. Each sample was weighed and soaked in the glass beaker containing 50 ml of $\text{NaHCO}_3/\text{NaOH}$ buffer solution with a pH of 10.5. The test was carried at $60\ ^\circ\text{C}$. The samples taken at specified times were washed with distilled water and dried in a vacuum oven at $50\ ^\circ\text{C}$ for 12 hr and weighed.

3. Results and discussion

PLA and LPB were reactively blended in the presence of a peroxide radical initiator. Scheme 1 describes the possible mechanism during the reactive blending. First, thermal decomposition of the DCP produces the cumyloxy radicals ($\text{RO}\cdot$). These highly reactive free radicals can abstract hydrogens from the PLA and LPB or can be added to the double bonds of the polybutadiene to produce macromolecular free radicals. The LPB macromolecular radicals can be combined to form internal crosslinking in the LPB matrix while the combination between the PLA and LPB radicals might produce the interfacial grafting between the two phases(Lim et al. 2016).

The radical initiator enhanced dispersibility of the rubber phases in the PLA matrix and solidified the liquid rubber through crosslinking to improve the toughness of the PLA. Besides, the WAXD patterns and DSC thermograms for the PBRs reveals that the radical induced reactive-blending apparently increased crystallization rate without any remarkable changes in crystallinity. The morphology of the rubber phases was significantly changed through the reactive-blending, illustrating that the compatibility between PLA and LPB is apparently enhance and the rubber particles were homogeneously dispersed at the nanoscale in the PLA matrix. The changes in the

conformational structure enhanced the toughness of the rigid PLA. The tensile strength of the PBRs slightly reduced and even marginally increased for the PBR03 and the elongations, in particular, are remarkably improved by more than 1,600% compared to the pure PLA.



Scheme 1. Mechanism of the reactive blending of LPB in PLA matrix.

4. CONCLUSIONS

Poly(lactic acid) (PLA) was toughened by a liquid rubber, polybutadiene (LPB). The toughened PLAs were prepared by melt-blending the PLA with various contents (0, 3, 6, and 9 wt.%) of the LPB and following reactive-blending in the presence of dicumyl peroxide (DCP), a radical initiator. In conclusion, the toughness of the rubber-modified PLA was significantly enhanced through the reactive blending, which is promising for the practical application of the toughened PLA in the area of packaging.

Acknowledgements

The work was financially supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science and ICT, Korea (NRF-2017R1A2B3012961; Brain Korea 21 Plus Program (21A2013800002)).

REFERENCES

- Choi, K.M., Choi, M.C., Han, D.H., Park, T.S., Ha, C.S. (2013), "Plasticization of poly(lactic acid) (PLA) through chemical grafting of poly(ethylene glycol) (PEG) via in situ reactive blending," *Eur. Polym. J.*, **49**, 2356-2364
- Lim, S.W., Choi, M.C., Jeong, J.H., Park, E.Y., Ha, C.S.(2016), "Toughening poly(lactic acid) (PLA) through *in situ* reactive blending with liquid polybutadiene rubber (LPB)," *Comp. Interf.*, **23**, 807-818.