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Improving Mechanical Properties of Poly-β-Hydroxybutyrate-co-β-Hydroxyvalerate by Blending with Natural Rubber and Epoxidized Natural Rubber

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Abstract. Poly-β-hydroxybutyrate-*co*-β-hydroxyvalerate (PHBV) is a bacterial-synthesized biopolymer. Moreover, PHBV is a biodegradable, it is an interesting biopolymer for disposable products. PHBV is difficult to process due to its low toughness, an elastic polymer such as natural rubber is introduced to develop toughness. In this experiment, PHBV mechanical properties were improved by blending with natural rubber (NR) and epoxidized natural rubber (ENR). The NR/PHBV and ENR/PHBV blends with the same ratio of 10/90 (wt/wt) could be extruded, whereas other conditions could not. This ratio was then used throughout this study to examine effect of maleic anhydride (MA) and benzoyl peroxide (BPO) to improve toughness of the blends. Result showed at composition where 1.0 % (wt/wt) MA and 0.05 % (wt/wt) BPO was mixed (coding EPMB2), several aspects of mechanical properties were improved. The blend, EPMB2 revealed the highest impact strength, significantly improved of elongation but drastically decreased of tensile strength. Storage modulus slightly decreased, tangent delta significantly increased when compared with neat PHBV.

Introduction

Polyhydroxyalkanoates (PHAs) is a biodegradable polymer. It has high crystallinity that makes it brittle. Blending PHBV with natural rubber (NR) could improve mechanical properties of PHBV. However, blending PHAs and NR is incompatible, NR is hydrophobic whereas PHAs is hydrophilic. Many attempts have been examined to develop compatibility of PHAs and NR by using compatibilizer and modifying of natural rubber such as epoxidized natural rubber (ENR).

Blending technology, many efforts attempted to improve mechanical properties of PHAs by blending PHAs with PLA [1-4] and propylene carbonate [5,6]. Using maleated polybutadiene as a compatibilizer for blending PHB with NR and ENR exhibited good compatibility and improved toughness [7]. This research focuses on improving toughness of poly-β-hydroxybutyrate-*co*-β-hydroxyvalerate (PHBV) which is a class of PHAs by blending with NR. The modified rubber such as ENR was also investigated. In order to enhance compatibility of PHBV and NR leading to improve mechanical properties of PHBV, the compatibilizer loading content such as maleic anhydride was examined.

Materials and Method

Materials. Poly-β-hydroxybutyrate-*co*-β-hydroxyvalerate (PHBV, ENMAT Y1000) was purchased from Ningbo Tianan Biologic Material Co. Ltd., China. NR bail grade STR 5L and ENR with 50% epoxidation level was purchased from Kij Paiboon Chemical Ltd., Thailand. Maleic anhydride (MA), was manufactured by Junsei Chemical Co. Ltd., Japan. Benzoyl peroxide (BPO), was manufactured by Alfa Aesar (A Johnson Matthey Company), South Korea.

Preparation of the Blends. The NR/PHBV blends were examined with following ratios (wt/wt): 10/90, 20/80 and 30/70, MA with 1.0 % (wt/wt) was added in all blends. The ENR were examined with the same conditions. The formulation of the blends (Table 1) were mixed by a twin-screw extruder (Bautex, BA-19, Korea) with a screw diameter of 19 mm and L/D ratio of 40. Barrel temperature was in range of 140 to 172 °C. Screw speed was 50 rpm. After blending, strand extrudate was cut into pellets to use for examining morphological and mechanical properties.

Table 1 Formulation of the NR/PHBV and ENR/PHBV blends.

NR/PHBV	MA (% wt/wt)	BPO (% wt/wt)	ENR/PHBV	MA (% wt/wt)	BPO (% wt/wt)
NPMB1	0.5	0.05	EPMB1	0.5	0.05
NPMB2	1.0	0.05	EPMB2	1.0	0.05
NPMB3	5.0	0.05	EPMB3	5.0	0.05

Morphology. Morphology of neat PHBV and the blends were investigated with Scanning Electron Microscope (Mini SEM: nano eye, Korea).

Mechanical properties. The samples were prepared by injection molder (Bau Technology, Korea) with mixing speed 60 rpm at 175 ^{o}C for 5 min. Samples were then subjected to impact and tensile testing protocol and evaluated their behavior. Izod impact tests were performed according to ASTM D256 on a plastic impact tester (Daeyeong, Korea). Elongation at break, tensile strength and Young's modulus were examined according to ASTM D 638 on a Universal Testing Machine (Zwick).

Dynamic Mechanical Analysis. Storage modulus and tangent delta were determined on a Dynamic Mechanical Analyzer (DMA Q800, TA Instrument Korea). The DMA was run in the dual cantilever mode over a temperature range of -50 ^{o}C to 150 ^{o}C at a scanning rate of 5 ^{o}C per minute and using a frequency of 1Hz.

Results and discussion

Compatibility of the blends. During extrusion, NR/PHBV and ENR/PHBV blends with ratio 10/90 could be processed, whereas the others could not; 20/80 and 30/70. Figure 1 presents SEM micrograph of fractured surfaces. The SEM results of NR/PHBV and ENR/PHBV blends with ratio 10/90 (Figure 1A and 1D, respectively) exhibited small particles of rubber distributing in PHBV matrix. Therefore, this optimum ratio was used for studying to improve mechanical properties.

Mechanical Properties. Table 2 demonstrates mechanical properties of neat PHBV and the blends. EPMB2 exhibited the highest impact strength. In case of NR/PHBV blend, impact strength could not be improved.

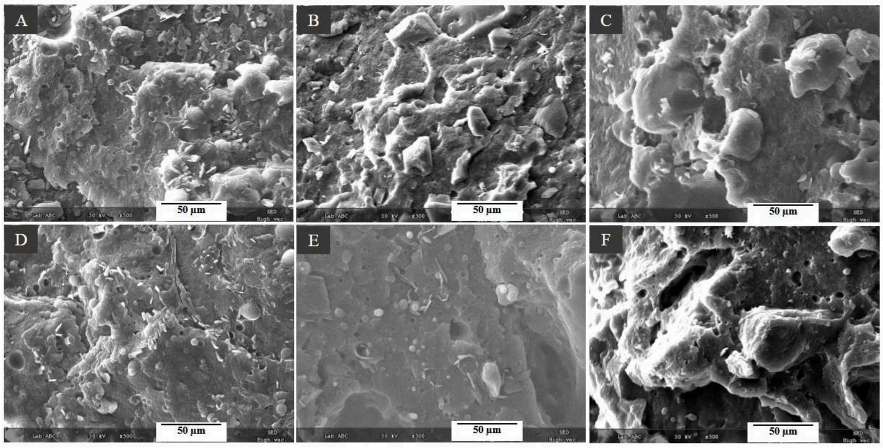

Fig 1 SEM micrographs of fractured surface of NPMB1 (A), NPMB2 (B), NPMB3 (C), EPMB1 (D), EPMB2 (E), and EPMB3 (F) (magnification × 500).

Dynamic Mechanical Analysis. Storage moduli and tangent delta of neat PHBV and ENR/PHBV blends were revealed in Figure 2. At below T_g, EPMB2 exhibited the highest storage modulus (Figure 2A). All blends presented higher tangent delta than neat PHBV (Figure 2B). High tangent delta revealed crosslinking between PHBV and NR/ENR. Therefore, addition of MA and BPO could promote reaction to enhance compatibility of ENR/PHBV.

Table 2 Mechanical properties of neat PHBV and the blends.

Samples	Impact Strength (kJ/m^2)	Elongation at Break (%)	Tensile Strength (MPa)	Young's Modulus (MPa)
PHBV	8.5^{a}	1.6	36.4	5778
NPMB1	2.47 ± 0.37	5.56 ± 0.65	7.95 ± 0.65^{f}	2387.98 ± 362.2^{i}
NPMB2	8.29 ± 0.67^{abc}	13.24 ± 1.02	8.75 ± 1.21^{fg}	2500.81 ± 211.5^{ij}
NPMB3	9.08 ± 0.46^{b}	22.95 ± 2.16^{e}	11.48 ± 1.86^{g}	2848.86 ± 101.2^{j}
EPMB1	4.48 ± 0.67	17.82 ± 1.75^{d}	11.41 ± 1.17^{h}	2732.65 ± 234.5^{j}
EPMB2	12.48 ± 0.84	19.88 ± 1.87^{de}	13.15 ± 1.87^{h}	2808.32 ± 257.8^{j}
EPMB3	7.71 ± 0.46^{c}	26.44 ± 1.64	18.68 ± 0.58	4775.99 ± 167.9

Note: different letters indicated statistically significant difference

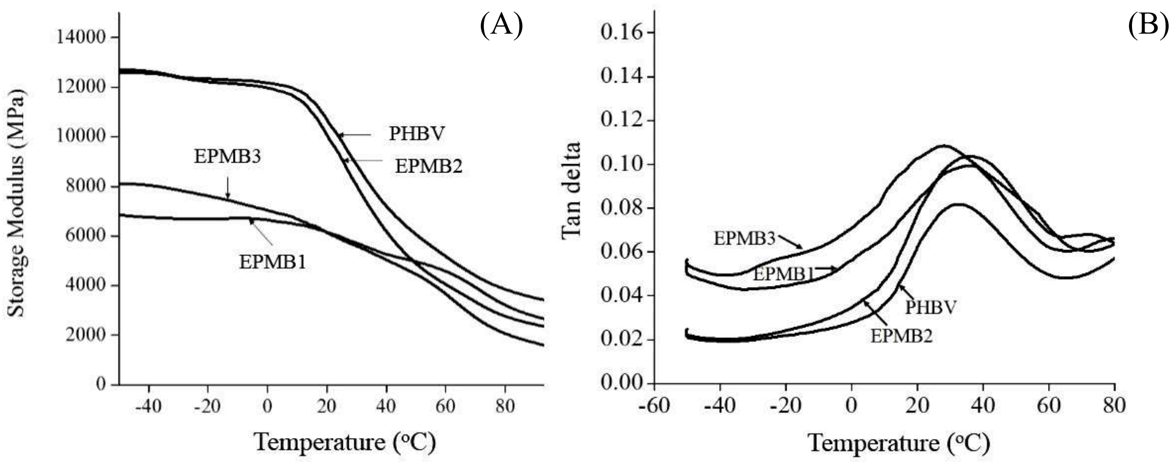

Fig 2 Storage modulus (A) and tangent delta (B) of the neat PHBV, EPMB1, EPMB2, and EPMB3.

Conclusion

In order to improve impact strength of PHBV by blending with NR or ENR, MA and BPO were needed to improve grafting. MA could improve compatibility by grafting onto the polymers backbone. Likewise, BPO generated free radical leading to an increasing grafting.

Addition MA with 1.0 % (wt/wt) and BPO with 0.05% (wt/wt) in ENR/PHBV blends (EPMB2) could improve impact strength and elongation at break. Storage modulus of EPMB2 slightly decreased, tangent delta significantly increased when compared with neat PHBV. Lower concentration of MA was required in ENR/PHBV blend comparing with NR/PHBV blends owing to an epoxy ring on ENR molecules reacting with PHBV directly.

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References

[1] Takagi, Y., R. Yasuda, M. Yamaoka, and T. Yamane, Morphologies and mechanical properties of polylactide blends with medium chain length poly(3-hydroxyalkanoate) and chemically modified poly(3-hydroxyalkanoate). J. Appl. Polym. Sci. 93 (2004) 2363-2369.

[2] Furukawa, T., H. Sato, R. Murakami, J. Zhang, I. Noda, S. Ochiai, and Y. Ozaki, Comparison of miscibility and structure of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)/poly(l-lactic acid) blends with those of poly(3-hydroxybutyrate)/poly(l-lactic acid) blends studied by wide angle X-ray diffraction, differential scanning calorimetry, and FTIR microspectroscopy. Polym. J. 48 (2007) 1749-1755.

[3] Gerard, T. and T. Budtova, Morphology and molten-state rheology of polylactide and polyhydroxyalkanoate blends. Eur. Polym. J. 48 (2012) 1110-1117.

[4] Zhao, Q., S. Wang, M. Kong, W. Geng, R.K.Y. Li, C. Song, and D. Kong, Phase morphology, physical properties, and biodegradation behavior of novel PLA/PHBHHx blends. J. Biomed. Mater. Res. Part B Appl. Biomater. 100B (2012) 23-31.

[5] Wang, X., S. Peng, and L. Dong, Effect of poly(vinyl acetate) (PVAc) on thermal behavior and mechanical properties of poly(3-hydroxybutyrate)/poly(propylene carbonate) (PHB/PPC) blends. Colloid. Polym. Sci. 284 (2005) 167-174.

[6] Corre, Y.-M., S. Bruzaud, and Y. Grohens, Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(propylene carbonate) blends: an efficient method to finely adjust properties of functional materials. Macromol. Mater. Eng. 298 (2013) 1176-1183.

[7] Parulekar, Y. and A.K. Mohanty, Biodegradable toughened polymers from renewable resources: blends of polyhydroxybutyrate with epoxidized natural rubber and maleated polybutadiene. Green. Chem. 8 (2006) 206-213.

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