

신규 PLA 컴퍼지트의 기계적 물성과 모폴로지 분석

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Novel Toughened Poly(lactic acid)-Based Blends: Physical and Morphological Properties

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초록: Polylactide(PLA)는 많은 소비용 상품을 위한 매우 이상적인 대체용 소재이다. 그러나 55도에서 65도 정도의 유리전이 온도(T_g)를 가지고 있는 PLA는 상온에서 매우 brittle한 특성을 가지고 있어서, 적용에 한계를 가지고 있는 실정이다. 본 연구에서는 PLA/acrylic elastomer 블렌드를 direct melt compounding를 통해서 제조하였고, 이 블렌드 내에 함유된 acrylic type에 따라, 유변학적, 형태학적, 물리적 성질을 고찰하였다. 다른 methyl methacrylate/butyl acrylate(MMA/BA) 조성을 가진 3 가지 종류의 acrylic rubber가 선정이 되었으며, PLA/acrylic 블렌드 조성물에서 vinyl acetate-ethylene가 어떻게 반응하는지 조사하기 위해서 상용화되고 있는 vinyl acetate-ethylene(VAE) copolymer가 binding agent로 사용되었다. 유변학적 분석을 통해서 acrylic elastomer는 PLA에 elastic 특성을 부가하여, 더 심한 가역적인 elastic 변형을 가지고 왔다. 한편, VAE는 PLA의 가공성을 향상시켰으며, DMA 분석을 통해서 PLA와 acrylic은 서로 상용성이 있는 블렌드를 형성한다는 것을 확인할 수 있었다. 형태학적, 기계적 물성 분석을 통해서 고무상인 poly(butyl acrylate)를 함유하고 있는 PLA-1 샘플이 PLA의 많은 단점을 개선하여 투명 포장재에 적용할 수 있는 좋은 대체용 소재라고 확인할 수가 있었다.

Abstract: Polylactide or poly(lactic acid) (PLA) is an ideal candidate for many consumer products. Unfortunately, with a glass-transition temperature (T_g) of 55 to 65 °C, PLA is too stiff and brittle for room-temperature applications; this greatly limits its use. In this work, PLA/acrylic elastomer blends were prepared via direct melt compounding. The rheological, morphological, and physical properties of the blends were evaluated as a function of acrylic type. Three types of acrylic rubbers were selected, which had different methyl methacrylate/butyl acrylate (MMA/BA) ratios. Additionally, commercial vinyl acetate-ethylene (VAE) copolymer was used as a polymeric binding agent to examine how VAE functioned in the PLA/acrylic blend system. Rheological analysis indicated that the acrylic elastomer made the PLA more elastic, leading to high reversible elastic deformation. On the other hand, VAE improved the processability of PLA. Dynamic mechanical analysis (DMA) showed that PLA and acrylics can form miscible blends. Morphological and mechanical tests proved that PLA-1, which contained the rubbery poly(butyl acrylate), is a good candidate to overcome some of the defects of PLA and may enable PLA-1 to be used in transparent packaging.

Keywords: poly(lactic acid), acrylic elastomer, vinyl acetate, blend, toughening.

Introduction

Polylactide or poly(lactic acid) (PLA) is an aliphatic polyester derived from corn, a renewable resource. PLA is a trans-

parent, semi-crystalline, thermoplastic material. It has relatively high strength and modulus, and is biocompatible and biodegradable. Therefore, PLA is an ideal candidate for food packaging and film wrap. Unfortunately, with a glass-transition (T_g) temperature of 55 to 65 °C, PLA is too stiff and brittle for room-temperature applications, which greatly limits its widespread use.^{1,2} For example, extruded film may be too brittle to handle in continuous processes.

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Great effort has been made to improve the ductility of PLA materials. Addition of a plasticizer can effectively decrease its stiffness and T_g . However, low molecular weight plasticizers migrate because of their high mobility within the PLA matrix.^{3,4} In contrast, high molecular weight plasticizers can phase-separate from PLA.⁵ Plasticization is thus limited for PLA. A more economic and practical approach to improve the ductility is to blend PLA with other flexible and elastic polymers. It has been blended with several biodegradable polymers, such as polybutylene adipate/terephthalate (PBAT),⁶ polybutylene succinate (PBS),⁷ and polyhydroxyalkanoates (PHA).⁸ Our research group has studied the effect of composition ratio on the thermal and physical properties of semi-crystalline polylactide/polyhydroxybutyrate-3-hydroxyhexanoate (PLA/PHB-HHx) composites and concluded that the toughness of PLA can be improved with the addition of small amounts of PHB-HHx.⁹ However, these rubbery biopolymers are relatively expensive, which increases the raw material cost of blends with PLA.

The addition of inexpensive non-degradable polymers has been explored to reduce the cost, improve the toughness, and expand the commercial opportunities. Poly(methyl methacrylate) (PMMA) is toughened by the addition of rubbery particles.¹⁰ Additionally, PLA/PMMA blends are miscible and might be expected to be transparent.¹¹ Cygan and Brake improved PLA mechanical properties by incorporating methyl methacrylate-butadiene-styrene (MBS) copolymer.¹² Fujii *et al.*¹³ investigated the blending of PLA and PMMA with a core-shell type of acrylic copolymer as an impact modifier. However, most of these blends showed only a limited improvement in the impact toughness. Additionally, their transparencies, an essential characteristic for packaging and other consumer products, were poor compared to pristine PLA.

Vinyl acetate-ethylene (VAE) copolymer is another versatile polymer. With increasing vinyl acetate (VA) content, this copolymer changes from a semi-crystalline thermoplastic material (low-density polyethylene, LDPE) into a rubbery and amorphous thermoplastic material (polyvinyl acetate, PVAc).¹⁴ The compatibility of PLA and VAE can be improved by adjusting the VA content of the copolymer, without the need for additional compatibilizers.¹⁵ Because of this unique property, VAE copolymers can act as polymeric binding agents and thereby modify the properties of polymer blends.

Recently, an innovative acrylic block copolymer, composed of methyl methacrylate (MMA) and butyl acrylate (BA), was developed. It is a thermoplastic elastomer possessing the trans-

parency of MMA and the toughness of BA.¹⁶ Considerable work has been devoted to blending PLA with other acrylic copolymers, e.g., poly(ethylene-*co*-glycidyl methacrylate),¹⁷ acrylonitrile-butadiene-styrene copolymer,¹⁸ and core-shell type particles.¹⁹ However, little attention has been paid to PLA/acrylic block copolymer (MMA-*co*-BA) blends. Furthermore, to the best of the authors' knowledge, only rather limited investigations have been reported concerning the effect of VAE on the properties of PLA/acrylic polymeric blends.

In this work, PLA/acrylic copolymer composites were prepared via direct melt compounding. The rheological, morphological, and physical properties of the composites were evaluated as a function of the type of acrylic copolymer. Three types of acrylic copolymer were selected, which had different MMA/BA ratios. Additionally, commercial VAE copolymer was added as a polymeric binding agent to evaluate how VAE functions in PLA/acrylic blends. We hypothesized that PLA, which is naturally hard and brittle, when compounded with the more ductile acrylic copolymer, would effectively balance the shortcomings of the individual polymers. Moreover, it was anticipated that PLA blended with commercial rubbery polymers could further expand the use of bio-friendly resources in a variety of applications, such as flexible films and food packaging.

Experimental

Materials and Sample Preparation. A commercial, linear, and amorphous PLA (Ingeo™, 4060D) was provided in pellet form by NatureWorks LLC (Blair, NE, USA). According to the supplier, the PLA had a density of 1.24 g/cm³ and a D-isomer content of about 12%. Acrylate copolymer (Kurarity, Kuraray, Japan) was used to toughen the PLA. Kurarity, used in this study, is block copolymer of methyl methacrylate (PMMA) and butyl acrylate (PBA). It is a thermoplastic elastomer possessing both PMMA's transparency and as well as PBA's elasticity. The chemical structures and technical data for the different grades of Kurarity are shown in Figure 1 and Table 1, respectively. VAE rubbers (Vinnex) with VA contents from

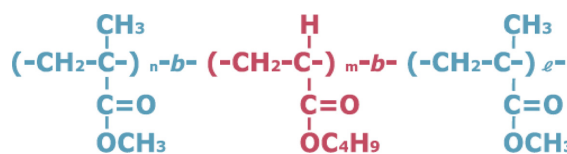


Figure 1. Chemical structure of acrylic copolymer.

Table 1. Data of Different Grades of Kurarity

Grade	Property	PMMA Con. (wt%)	Specific gravity	Hardness	Transmittance (%)	Modulus at 100% (MPa)
K-2330		20	1.08	32	91	0.3
K-2250		30	1.08	64	91	3.7
K-4285		50	1.11	95	91	19

Table 2. Main Sample Recipe of PLA-Based Blends

Recipe (wt%)	PLA 4060	K2330	K2250	K4285	Vinnex
Sample code					
PLA-1	50	50	-	-	-
PLA-2	50	-	25	25	-
PLA-5	50	30	-	-	20
PLA-6	50	-	15	15	20

80 wt% were kindly supplied by WACKER Chemical Co., Ltd.

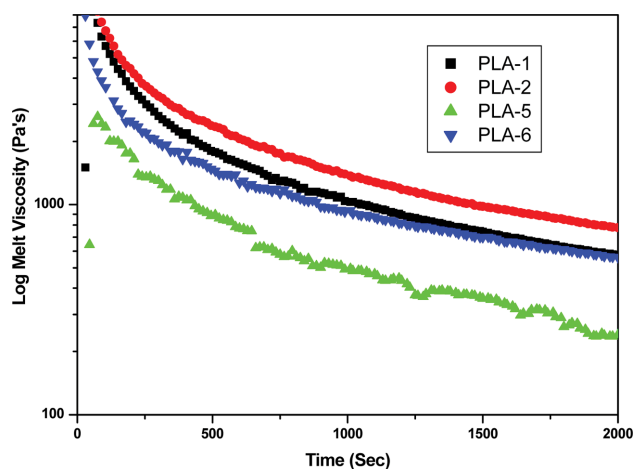
Melt blending was performed using a co-rotating twin screw extruder (Leistritz ZSE-18) having a screw diameter of 17.8 mm and an L/D ratio of 40. The screw speed was 150 rpm, and the melt-zone temperatures were 140, 155, 170, 180, 170, 160, 170, 180, 180, and 180 °C. All the samples were dried at 70 °C in a convection oven for 12 h before processing. PLA was manually premixed with other polymers by tumbling in a plastic ziplock bag and subsequently fed into the extruder for melt compounding. The extrudate was cooled in a water bath and then granulated by a pelletizer. The total content of PLA was fixed at 50 wt% for all the blends. Table 2 summarizes the recipes of the PLA-based blends. Pellets of the blends were then compression molded in a hydraulic compression press for 5 min at 180 °C at a pressure of 6000 psi.

Measurement. The rheological properties of the blend samples were measured using an advanced rheometric expansion system (ARES; Rheometric Scientific, Piscataway, NJ, USA) with parallel-plate geometry. The frequency was varied from 0.05 to 500 rad s⁻¹ with a 12.5-mm-diameter parallel plate with a 1.0 mm gap at 150 °C. Differential scanning calorimetry (DSC) data were obtained using a DSC 7 (Perkin-Elmer, Waltham, MA, USA). Samples (5 mg) taken from the central sections of test specimens were sealed in aluminum pans and heated from -40 to 200 °C at 5 °C/min followed by holding at 200 °C for 3 min before rapidly cooling to -40 °C. Samples were reheated to 200 °C at the same heating rate. The dynamic mechanical properties were measured on a dynamic mechanical analyzer (DMA 2980; TA Instruments, New Castle, DE,

USA) set in tension mode at a frequency of 1 Hz in a nitrogen atmosphere. Samples (15×5×0.5 mm) were cooled to -40 °C and then heated gradually to 200 °C at a rate of 2 °C min⁻¹. Mechanical tests were conducted at room temperature with a tensile testing machine (Instron 4465; Instron, Norwood, MA, USA) according to ASTM Standard D638. The crosshead speed was 10 mm min⁻¹. Dumbbell-shaped specimens, 3.5×14×0.3 mm (width×gage length×thickness), were tested. The values of 10 measurements were averaged, and the standard deviation (SD) was calculated. The morphologies of PLA-based blends were investigated by scanning electron microscopy (SEM) (JSM-6700F; JEOL, Tokyo, JP). Cross-sections of gold-coated specimens were examined after fracturing in liquid nitrogen. The light transmittance of neat PLA and PLA's blends sheet were measured with a UV-vis spectrophotometers instrument (721, Shanghai Jinhua Group Co., Ltd., China) in the range of 500-800 nm at room temperature.

Results and Discussion

Figure 2 shows the melt viscosities of the PLA-based blends. The melt viscosity decreased with increasing residence time at same temperature, indicating slow thermal degradation. The presence of oxygen and water can both significantly increase

**Figure 2.** Melt viscosities of PLA-based blends.

the degradation rate of polyesters such as PLA. In addition, for PLA-1 and PLA-5, the melt viscosity increased sharply at first, and then decreased with increasing residence time. As shown in Table 1, both PLA-1 and PLA-5 is mixed with PLA and K-2330, which has large amount of BA portion; about 80 wt%. That is to say, K-2330 has the most elastomeric property among other acrylic elastomer. Therefore, this result can be explained that the elastic rubber component cannot be dissolved and collapsed at early residence time. However, with the residence time, the rubber is abruptly dissolved and collapsed, resulting in the sudden decrease of melt viscosity. In other word, Both PLA-1 and PLA-2 had higher melt viscosities than PLA-5 and PLA-6 at all temperatures, indicating that incorporation of the VAE copolymer reduced the melt viscosity. The acrylic copolymers are more rubbery and flexible than the VAE copolymer. Hence, acrylic elastomers might be expected to make PLA more elastic, leading to high reversible elastic deformation of PLA melts. Furthermore, the low melt viscosity of the blend facilitated extrusion of the PLA. Because the melting point of VAE is much lower than that of PLA, the VAE melted in the first section of the extruder and then acted as a lubricant to help transfer the PLA pellets into the mixing zones. Consequently, the screw torque and extrusion pressure were reduced.

Figure 3 displays the second-heating DSC curves of the PLA-based blends. Neat PLA and the PLA-based blends did not display crystallization or melting peaks. These blends had a broad halo in their wide-angle X-ray scattering patterns (not shown), indicating that they were composed of amorphous polymers. Additionally, only one T_g peak was detected; it

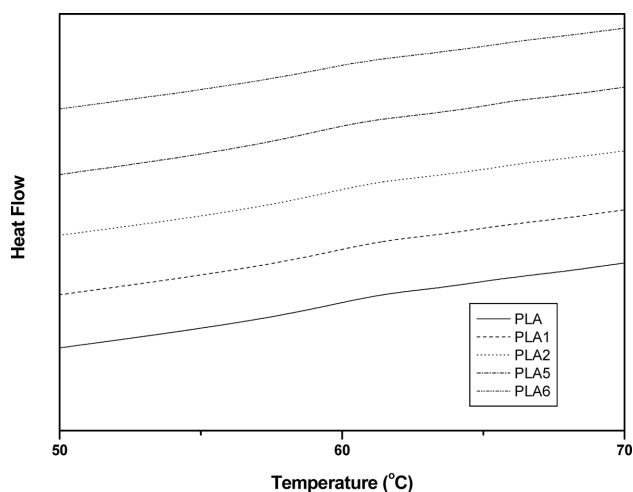


Figure 3. 2nd heating DSC curves of PLA-based blends.

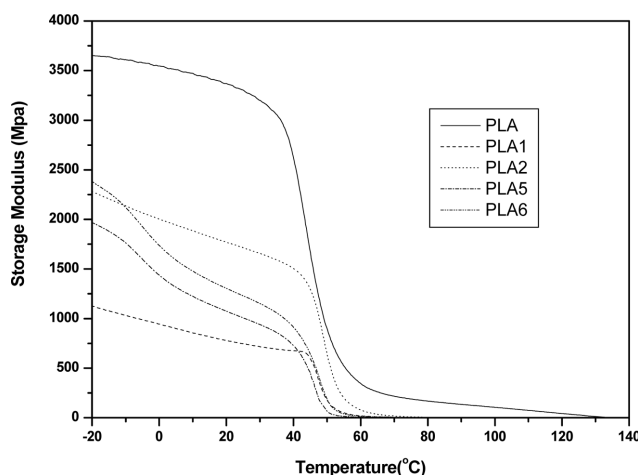


Figure 4. Storage modulus results of PLA and PLA-based blends.

occurred at about 55 °C and was attributed to PLA. This behavior indicated that PLA and other rubbery polymers may form compatible blends. DMA analysis provided further details of this compatibility.

Figure 4 shows the storage modulus of PLA and PLA-based blends as a function of temperature. The high modulus of PLA at room temperature indicates that PLA is brittle and stiff, because the storage modulus of a polymer is indicative of material stiffness under shear deformation.²⁰ The storage modulus decreased abruptly near 55 °C because of the glass transition of PLA. Both PLA-1 and PLA-2, which contained added acrylic elastomer, had lower storage moduli than neat PLA below the T_g . This indicated that the addition of acrylic polymers improved the ductility and toughness of PLA. The greatest degree of improvement was found for PLA-1. Poly(butyl acrylate) (PBA) is a very ductile (2000% elongation at break) and transparent rubbery material. PLA-1 blends were made using the acrylic copolymer having the highest PBA content (see Table 1). PBA improved the ductility of PLA more efficiently than did PMMA. PLA-5 and PLA-6, which incorporated the VAE copolymer, had storage moduli values between those of the PLA-1 and PLA-2 blends. This suggested that VAE may not be as effective as a stiffness modifier as the acrylics, possibly because of the less flexible vinyl acetate backbone of VAE.

Figure 5 displays the loss modulus curves of PLA and the PLA-based blends. The T_g is defined here as the temperature of the maximum of the loss modulus curve at the indicated frequency; it is associated with a relaxation process. Neat PLA has a T_g of about 55 °C. Regardless of the added polymers, the T_g of PLA did not shift to a lower temperature. Generally, plas-

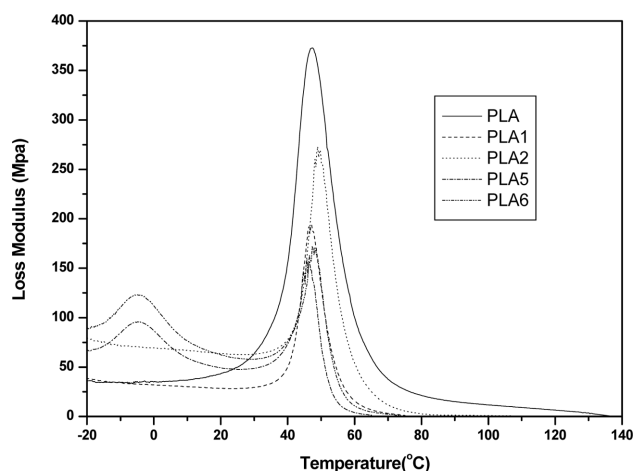


Figure 5. Loss modulus result of PLA and PLA-based blends.

ticizers lead to substantial reductions in both the T_g and mechanical properties because of efficient diffusion within the molecular chains.²¹ Moreover, the extent of this effect increases with increasing amounts of plasticizer. Therefore, acrylic and VAE copolymers did not behave as plasticizers in the PLA blends. Rather, their innate ductilities affected the viscoelastic properties of the blends.

In the case of PLA-5 and PLA-6, a broad peak related to the T_g of VAE gradually emerged near -7°C ; this was presumably due to poor miscibility of PLA and the VAE copolymer as well as phase separation. In contrast, the PLA/acrylic blends showed one T_g peak that was attributed to PLA. We therefore concluded that the acrylic copolymer was more miscible with PLA than VAE. Blending high-PBA-content acrylic polymer with PLA is a better choice for improving the mechanical properties, such as ductility.

Figure 6 shows SEM micrographs of PLA and the PLA-based blends. Neat PLA had a smoother surface. In the PLA-1 and PLA-2 blends, small domains of acrylic rubber were homogeneously dispersed within the PLA matrix; these domains were less than about $2\ \mu\text{m}$ in size. Additionally, the interface between the PLA and acrylic domains was vague, confirming that phase separation between the two components was not complete. There were many more aggregates in the PLA-5 and PLA-6 blends, some of which exceeded $5\ \mu\text{m}$. The pronounced aggregation and phase separation indicated that the compatibility between VAE and PLA was worse than that of the acrylics and PLA. The SEM analysis supported the DMA findings.

The optical clarity of a blend is another way to judge polymer miscibility: immiscible blends are usually cloudy or milky

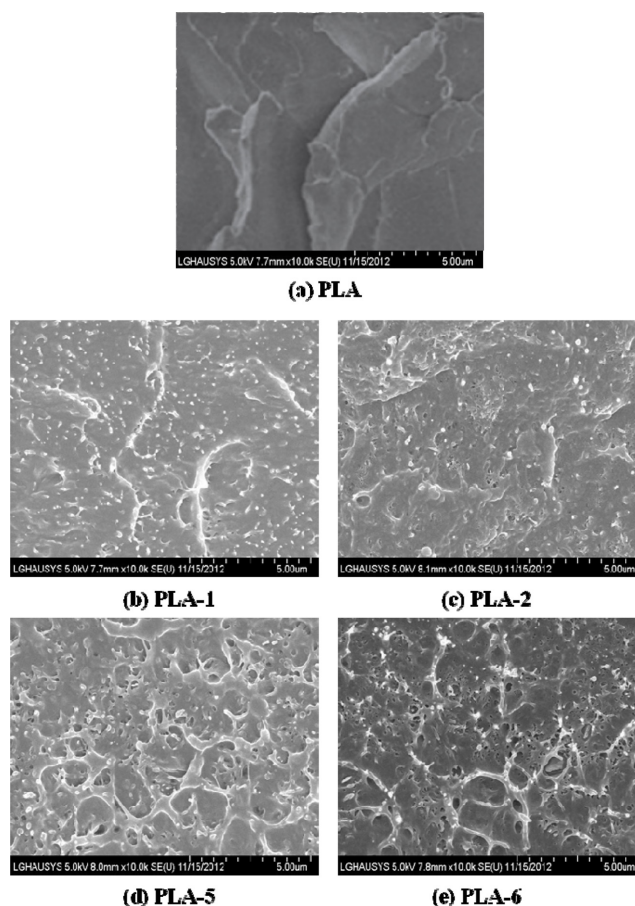


Figure 6. SEM images of PLA and PLA-based blends.

white because of the different refractive indices of the components.²² Figure 7 shows optical photographs of 1.5-mm-thick films of PLA and PLA blends. The PLA sheet was completely transparent, and the PLA-1 and PLA-2 films were also highly transparent. However, the blends containing VAE were not as clear as the other blends. To further study the effect of rubbery polymers on the transparency of the PLA, we measured the visible light transmittance of PLA and PLA-based blends using an ultraviolet-visible spectrophotometer, which is displayed in Figure 8. The transmittance decreased with increasing VAE content, consistent with the optical observations. The PLA-based blends containing the acrylic rubbers were highly transparent and ductile and met the requirements of transparent packaging materials.

The stress-strain curves of the PLA-based blends are shown in Figure 9, and details of the mechanical properties are given in Table 3. The tensile fracture behavior changed from brittle for neat PLA to ductile for the PLA-based blends; the neat PLA was very rigid and brittle, so it is very difficult to drawing

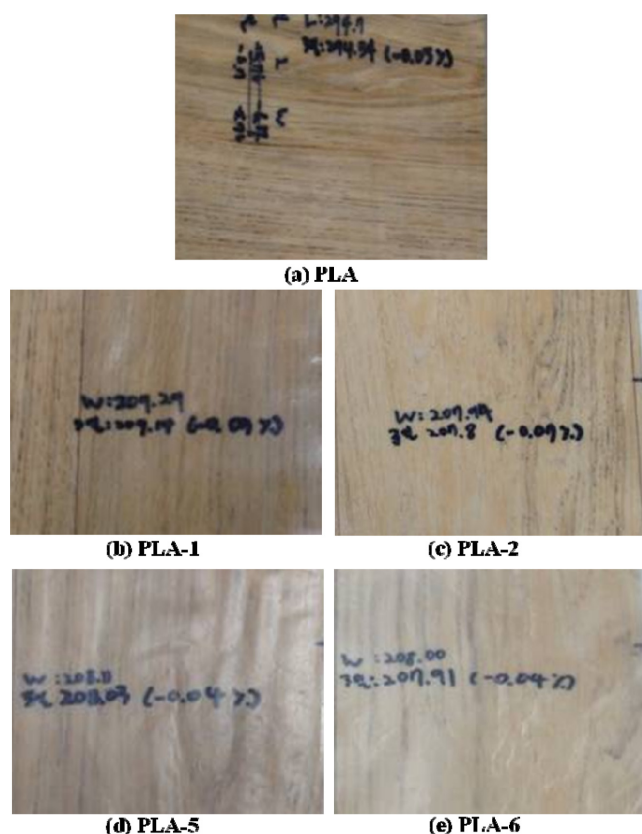


Figure 7. Photographs of the PLA and PLA/PBA blends sheets (1.5 mm thickness).

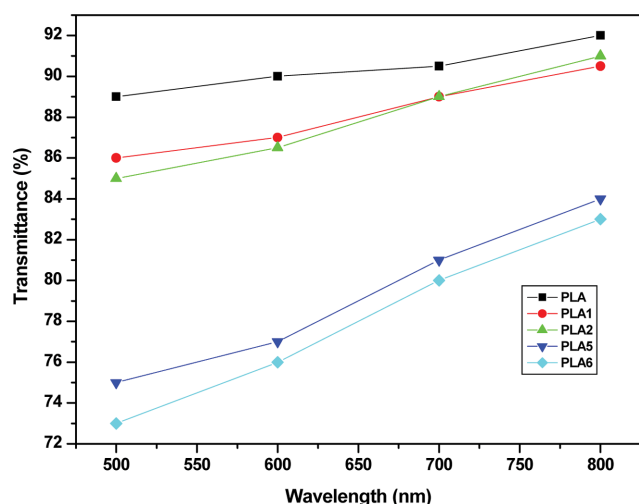


Figure 8. Comparison of transmittance in the PLA and PLA-based blends.

the plot including PLA result. In tensile tests, strain softening may stimulate strain localization, which causes the buildup of local, multi-axial stresses. If the local strain is not delocalized, it induces void nucleation and the formation of cracks in the

Table 3. Mechanical Properties of PLA and PLA-Based Blends

Property \ Sample	PLA	PLA-1	PLA-2	PLA-5	PLA-6
Tensile strength (MPa)	45.63.2	17.12.1	24.62.1	16.73.1	21.33.2
Elongation at Break (%)	3.60.5	2373.4	2654.5	2023.7	2114.1

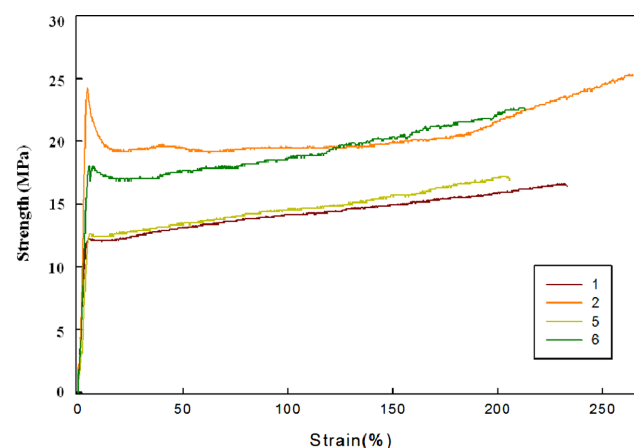


Figure 9. Stress-strain curves of PLA-based blends.

matrix, which lead to a brittle failure behavior. Apparently, neat PLA had a strong strain softening that was not stabilized by strain hardening. In contrast, the blends containing the rubbery polymers showed stable neck growth and strain hardening, indicating that these polymers improved the ductility of the PLA. The stress-strain curve after the yield point displayed a combination of strain softening and cold drawing. In this region, there was competition between the orientation of the PLA chains and crack formation. Hence, there was a drop in stress with increasing strain. Compared with PLA-1 and PLA-2, however, the strain hardening of PLA-5 and PLA-6 could not be weakened, implying that the acrylics improved the ductility of PLA better than the VAE polymers. This behavior can be explained by two factors. First, the miscibility of PLA and VAE was lower than that of PLA and the acrylics. Second, vinyl-acetate, the backbone in VAE, may not have sufficient rubberiness and ductility to overcome PLA's brittleness. PLA-1, which contained the rubbery PBA, improved the physical property deficiencies of PLA and could enable its use in transparent packaging.

Conclusions

Bioplastic blends of PLA, acrylics, and VAE were prepared

by melt-mixing. The mechanical properties and surface morphologies were investigated. The conclusions of the study are as follows:

1. Incorporation of acrylic elastomers improved the elasticity of PLA, leading to high reversible elastic deformation. VAE improved the extrudability of PLA.

2. PBA, a very ductile and transparent rubbery material, was better than PMMA at improving the ductility of PLA.

3. Acrylic copolymer was more miscible than VAE with PLA. Blending an acrylic polymer having a high PBA content with PLA was particularly effective at improving the properties of PLA, including ductility.

4. PLA-1, which contained the rubbery PBA, improved the deficiencies of PLA. PLA-1 would be suitable for transparent packaging.

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