Preparation and Characterization of Poly(lactide)

Having Improved Impact Resistance

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이 論文을 碩士學位 論文으로 提出함
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主審____________________

副審____________________

委員____________________
Abstract

Poly(lactide) (PLA) is an important biodegradable polymer derived from 100% renewable resources, such as corn. It has many advantages including biodegradability, excellent biocompatibility, processibility, and low energy dependence. In spite of many advantages, PLA has been used in limited the practical applications due to some inherent drawbacks. The major drawbacks of PLA are brittleness and low toughness. The above drawbacks could be overcome by enhancing their properties through copolymerization, blending and toughening techniques. The most widely employed method to modify the properties of polymer is to make blends.

In this study, in order to improve the impact strength of PLA, it was blended with modified poly(n-butyl acrylate) (PBA). Modified PBA was prepared by copolymerization of n-butyl acrylate and 2-hydroxyethyl methacrylate terminated oligo(L-lactide) (OLLA). The chemical structure of the copolymer was confirmed by $^1$H-NMR. The effect of the addition of up to 10 phr of the modified PBA on the mechanical properties of blends was investigated by UTM and Izod impact tester. The Izod-fractured surfaces were examined by SEM to study the
fracture mechanism of the blends. In addition, thermal properties of blends were characterized by TGA.

Keyword: poly(lactide), poly(n-butyl acrylate), blending, impact strength
국 문 요 약

폴리유산은 지방족 폴리에스터 고분자의 하나로서 전분에서 얻어지는 유산을 원료로 하여 제조되는 자연 순환형의 생분해성, 생체적합성 고분자이다. 다른 생분해성 고분자와는 달리 대량 생산이 가능하며 범용고분자 재료의 기본 특성을 지니고 있어 생체 재료와 같은 기능성 분야뿐만 아니라 범용분야에서도 사용이 가능하다. 그러나 높은 결정화도로 인해 나타나는 brittle 한 물성으로 인하여 유연성이 요구되는 소재로는 응용상 문제가 있으며 낮은 열안정성으로 인해 용융 가공 시 급격한 분자량 감소를 유발하여 기계적 특성이 멀어지는 단점을 지니고 있다. 이와 같은 단점들은 공중합, 블렌딩 그리고 충전체의 점가 등과 같은 방법으로 물성을 향상시킴으로써 극복할 수 있으며, 이런 방법들은 중에서 가장 널리 이용되는 방법은 다른 고분자와의 블렌딩을 통해 물성을 향상시키는 것이다.

본 연구에서는 폴리유산의 단점으로 지적되고 있는 brittle 한 성질을 감소시키기 위하여 충격강도를 향상시키는 목적으로 널리 사용되고 있는 폴리부틸아크릴레이트를 개질하고 이를 폴리유산과의 블렌딩함으로서 충격강도를 향상시키는 등 물성을 개선하고자 하였다.

Keyword: 폴리유산, 폴리부틸아크릴레이트, 블렌딩, 충격강도
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1. INTRODUCTION

Recently, research in biodegradable polymers has attracted much attention, because of their wide range of application in biomedical, packaging, and agriculture field.[1] One of the most important biodegradable polymers is poly(lactide) (PLA), which is a linear aliphatic polyester derived from renewable resource such as corn and sugar.[2] Until the last decade, the main uses of PLA have been limited to medical applications such as implant devices, tissue scaffolds, and internal sutures, because of its high cost, low availability, and limited molecular weight.[3] New techniques which allow economical production of high molecular weight PLA polymer have broadened its uses in recent.[4] Since PLA is compostable and derived from sustainable source, it has been viewed as a promising material to reduce the solid waste disposal problem.[5-6] Also, PLA has become an ideal material for food packaging and other consumer products due to its low toxicity and its eco-friendly characteristics.[7-8]

PLA development initiated with the lactide production formulas published by Bischoff and Walden in 1893. In 1932, Carothers and coworkers produced low molecular weight PLA. E.I. DuPont de Nemours and Ethicon, Inc. began marketing PLA in medical

PLA has many advantages such as eco-friendly, excellent biocompatibility, processibility, and less energy dependence.[11-15] In spite of many advantages, PLA has been limited to use the practical application. Because PLA has some drawbacks. The major drawbacks of PLA are brittleness and low toughness.[16-17] Several bulk-modification methods have been employed to improve mechanical properties, degradation behavior, processibility and crystallinity of PLA.
Among various methods for modifying PLA, such as blending PLA with immiscible and miscible polymers is a more practical and economical way of toughening PLA. Hillmyer et al. blended PLA with low density poly(ethylene) (LDPE) to improve the toughness.[18-19] PLA crystallinity was found to significantly impact the blend toughness. Amorphous PLA blends with LDPE needed PLA–LDPE diblock copolymer compatibilization, however, semi-crystalline PLA blends with LDPE showed toughening even in the absence of the block copolymer. PLA–poly(vinyl acetate) (PVAc) blends were found to be miscible, exhibited improved tensile strength between 5 and 30 wt% PVAc, and improved elongation at break with 5wt% PVAc.[20] Zhang et al. studied crystallization and phase behavior of poly(methyl methacrylate) (PMMA)–poly(dl-lactide) blends and found that blends prepared by a solution/precipitation method were miscible while those prepared by a solution casting were partially miscible.[21] They also found that the crystallization of poly(dl-lactide) was greatly restricted by amorphous PMMA.

Recently, DuPont has commercialized Biomax® Strong PLA additives to improve toughness without significant transparency loss. These additives are designed to have ‘special chemistry’ for PLA, so
even small amounts (1–5 wt%) provide significant toughness benefits. NatureWorks LLC studied different commercial toughening agents for PLA. In their work, Blendex™ 338, an acrylonitrile–butadiene–styrene terpolymer containing 70% butadiene rubber, was found to significantly improve notched Izod impact strength and elongation at break of PLA. Another additive, Pellethane™ 2102-75A (a commercial grade polyurethane from Dow Chemical Company), was also found to significantly improve these properties.

Another approach to improve the mechanical properties of PLA is through the incorporation of organic/inorganic fillers. For example, PLA–clay solvent cast blends exhibited improved Young’s modulus.[22] PLA blends with β-Ca(PO₃)₂ exhibited a modulus of elasticity similar to that of natural bone (>5 GPa).[23] PLA has also been blended with metal oxides, such as alumina and titania, to improve mechanical properties suitable for orthopedic applications.[24-27] Carbon-fiber-reinforced PLA composites showed improved mechanical properties on nitric acid surface treatment of the fibers.[28] Additionally, PLA has been melt blended with inorganic fillers, such as 9Al₂O₃, 2B₂O₃ and CaCO₃, to improve its mechanical and thermal properties.[29] PLA-nano-sized precipitated calcium carbonate (NPCC)
composites showed a strain at break increase from less than 5% for neat PLA to 5.1% at 2.5 wt% NPCC content to 13% at 5 and 7.5 wt% NPCC contents. PLA-organically modified montmorillonite (MMT) clay composites showed a strain at break increase to 15.9% at 2.5 wt% MMT content. The tensile strength of PLA–NPCC composites decreased monotonically with NPCC content from 65MPa for neat PLA to 57 MPa at 7.5 wt% NPCC content, whereas that of PLA–MMT composites increased to 67 MPa at 5 wt% MMT content and then decreased to 55MPa at 7.5 wt% MMT content. The extent of increase in strain at break and decrease in tensile strength was not significant in that study.[30]

In this study, order to improve PLA’s impact strength, PLA was blended with modified poly(n-butyl acrylate) (PBA). Modified PBA was prepared by copolymerization of n-butyl acrylate and 2-hydroxyethyl methacrylate terminated oligo(L-lactide) (OLLA). The chemical structure of the copolymer was confirmed by $^1$H-NMR. The effect of the addition of up to 10 phr of the modified PBA on the mechanical properties of blends was investigated by UTM and Izod impact tester. The Izod-fractured surfaces were examined by SEM to
study the fracture mechanism of the blends. In addition, thermal properties of blends were characterized by TGA.
2. EXPERIMENTAL

2. 1. Materials

Poly(lactide) (PLA) (4032D) was provided by NatureWorks LLC with the molecular weight of $M_w = 200,000$. n-butyl acrylate (nBA) and 2-hydroxyethyl methacrylate (HEMA) were purchased Sigma Aldrich and distilled under vacuum. L-lactide (LLA) was supplied from Purac and recrystallized from ethyl acetate. Tin(2) 2-ethylhexanoate (Sn(Oct)$_2$) and 1,4-dioxane were obtained Sigma Aldrich and used without purification. 2,2’-azobisisobutyronitrile (AIBN) was recrystallized from methanol.

2. 2. Synthesis of HEMA-OLLA macromonomer

Macromonomer of HEMA terminated OLLA was synthesized by ring-opening polymerization of LLA with HEMA as initiator in the presence of Sn(Oct)$_2$ as catalyst. In order to precisely control the lactide chain length, feed molar ratios of LLA/HEMA were adjusted to 14:1. A mixture of LLA and HEMA were added into the three neck-flask and heated up to 150 °C, under nitrogen purging for complete melting. Catalytic amounts of Sn(Oct)$_2$ (0.007 mol-% with respect to LLA) dissolved in toluene were added to the mixture. Immediately after
degassing for 1 h, the mixture was sealed under vacuum and maintained at 150 °C for 24 h and then allowed to cool down to room temperature. The mixture was dissolved in dichloromethane, precipitated three times in cold methanol with vigorous stirring, and dried under vacuum.

2. 3. Synthesis of A-OLLA copolymer

Copolymerization of poly(butyl acrylate-co-hydroxyethyl methacrylate-g-lactide) (A-OLLA) was carried out in 1,4-dioxane with AIBN as an initiator by free radical copolymerization. HEMA-OLLA were combined with freshly distilled BA in 1,4-dioxane under nitrogen purging and stirred for homogeneous mixing. AIBN was added and the mixture kept at 80 °C for 1 h. After polymerization, the mixture was allowed to cool down to room temperature and precipitated three times in n-hexane. Then the copolymer was dried under vacuum.

2. 4. Preparation of PLLA/A-OLLA blends

In order to prevent any potential hydrolytic degradation of the biodegradable polymer during melt processing, PLA and A-OLLA were dried in the vacuum oven at 60 for 6 h before melt processing. PLA/A-
OLLAs were prepared by twin-screw extruder with a screw diameter of 19 mm and a die length/die diameter (L/D) ratio of 40. The twin screw extruder was independently operated with eight different temperature zones of respective temperature range from 170 to 190, feeding zone at 160 and die section at 200 with the screw speed of 150 rpm. The melted samples were quenched in water bath and pelletized.

2.5. Characterization

The chemical structures of the macromonomer and copolymer were confirmed by nuclear magnetic resonance spectroscopy (\(^1\)H-NMR, Varian Inova 400, at 400 MHz). Chemical shifts were measured in ppm using tetramethylsilane (TMS). Molecular weights and molecular weight distribution (Mw/Mn, PDI) were obtained with gel permeation chromatography (GPC, Water Breeze HPLC System). Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1.0 ml/min. Tensile strength and Young’s modulus were measured under the uniaxial elongation at room temperature in accordance with ASTM D638 by using universal testing machine (UTM, Hounsfield Test Equipment). Each sample was provided with as a dog-bone type and the resulting value was at least an average of at least five measurements. The
dynamic mechanical properties of blends were investigated using a dynamic mechanical analysis (DMA, TA instruments Q800). A frequency of 1 Hz and amplitude of dynamic deformation of 30 µm were carried out in a Multi-stress-strain mode. Samples were heated from room temperature up to 120 °C with a heating rate of 3 °C/min. Notched Izod test (Water 410 T50) of blends were performed in accordance to the ASTM D256 at room temperature.

The morphologies of the fracture surfaces were observed using field emission scanning electron microscopy (FE-SEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV after the samples were pre-coated with a homogeneous Pt layer through ion sputtering (E-1030, Hitachi, Japan).
3. RESULT AND DISCUSSION

3.1. Synthesis of HEMA-OLLA macromonomer and A-OLLA

A schematic synthetic procedure of HEMA-OLLA macromonomer and their copolymerization with BA to produce A-OLLA is illustrated in Figure 1.

$^1$H-NMR spectrum of HEMA-OLLA macromonomer is shown in Figure 2(a). It is interesting to stress the fact that, in addition to the resonance signals of the methacrylic double-bond hydrogens at 5.59 and 6.11 ppm, only one sharp multiplet centred at 4.34 ppm can be distinguished, and it is assigned to the four hydrogens of the oxyethylene residue. The $\alpha$-CH$_3$ protons of the methacrylic HEMA residue give a sharp triplet at 1.93 ppm. And then, from the $^1$H-NMR spectrum, it was possible to determine the degree of polymerization (DP) for an average lactide chain length in the polyester segment and subsequently, its number average molecular weight. The relative peak intensity ratio of methyl protons of OLLA to methyl protons of the HEMA end group was used to calculate DP of the OLLA chain. Table 1 summarizes the molecular weight of the macromonomer as determined by NMR and gel permeation chromatography (GPC).

A-OLLA synthesized by free radical copolymerization were
characterized in terms of confirmation of product and molecular weight by $^1$H-NMR and GPC, respectively. It can be seen in Figure 2(b) that the resonance signals of the methacrylic double-bond hydrogens at is not determined. This is understandable since HEMA-OLLA is successfully copolymerized with BA.

3.2. Mechanical properties of PLA/A-OLLA blends

Tensile properties of neat PLA and PLA/A-OLLA blends are shown in Figure 3(a)-(b). The main tensile properties such as tensile stress and Young’s modulus are presented in Table 2. The tensile strength and modulus of PLA decreased almost linearly with increasing A-OLLA content. Tensile strength and modulus decreased by 30.9 and 42.7 %, respectively, by adding 10 phr A-OLLA in the blends. The lower tensile strength and modulus of A-OLLA compared to those of neat PLA produced this anticipated result. As the concentration of A-OLLA increases, it becomes the dominant component of the blend, and the compounds become softer and flexible, with a lower tensile strength and modulus.

The impact strength of neat PLA and PLA/A-OLLA blends is shown in Figure 3(c) and presented in Table 2. For each composition, A-
OLLAA incorporation increased the notched Izod impact resistance over that of neat PLA (1.44 kgf-cm/cm). The smallest increase was seen with addition of 1 and 3 phr A-OLLAA (2.67±0.06 kgf-cm/cm and 2.98±0.21 kgf-cm/cm). An intermediate impact values of 3.91±0.06 kgf-cm/cm was observed for the 5 phr A-OLLAA composition. The highest impact values for blends in this study were 6.13±0.07 kgf-cm/cm, which were obtained for 10 phr A-OLLAA composition.

It should be noted that the modified PLA maintains quite high tensile modulus and tensile strength with the obviously increased impact strength, which means that the obtained material having a good toughness balance.

3.3 Mechanism of toughening and morphology of impact fractured surface

Several studies have reported occurrence of various energy-dissipative mechanisms locally in a stressed specimen before crack development. Mechanisms such as crazing, bond rupture, cavitation, crack growth, plastic and viscoelastic deformations, etc., relieve stresses and consequently reduce the stored elastic energy. High strength and toughness therefore, result primarily from special
combination of these mechanisms that retard or arrest the growth of cracks.[31] Using fractured surfaces of notched Izod impact tested samples as a means of differentiating brittle to ductile fractures, previous studies reported noticeable whitening only occurs at the origin of the notched tip for brittle fracture, while ductile fracture involves all of the material around the fractured surface in stress whitening and forms a yielding zone.[32] In rubber-toughened plastic systems two types of cavitation induced by impact or tensile tests are discerned, which includes internal cavitation in the rubber domains for the blends with strong interfacial adhesion and debonding cavitation between the interfaces with not enough interfacial adhesion.[33] Generally, the mechanisms causing damage during brittle fracture have been prescribed as mainly crazing or microcracks and cavitation.[34] Crazing, cavitation, shear banding, crack bridging and shear yielding reportedly occur as important energy dissipation processes involved in the impact fracture of toughened polymer systems.

SEM images of the notched impact fractured surfaces of neat PLA and PLA/A-OLLA blends are shown in Figure 4. The surfaces of fractured neat PLA and PLA/A-OLLA blending samples with up to 3 phr A-OLLA remained relatively flat and smooth without any signs of
plastic deformation, which are typical characteristics of brittle failure. Moreover, evident cavitation caused by debonding and stress whitening near the notched tip due to crazing/microcracks resulted. Although debonding absorbs a considerable amount of fracture energy, a limited effect resulted in these samples due to a low concentration of A-OLLA used in the blends (up to 3 phr), which caused mainly the matrix to bear most of the stress. These results corroborate the notched Izod impact strength data illustrated in Figure 3(c), where the addition of up to 3 phr A-OLLA into PLA did not toughen the matrix.

By contrast, as can be seen in Figure 4(c)-(d), the fractured surface of blending samples with 5 or more A-OLLA are rough, which are sign of improved toughness and ductility. It suggests that the impact specimen should be broken through the yielding of the matrix.

3. 4. Dynamic mechanical property of PLA/A-OLLA

In binary system, glass transition temperature ($T_g$) can be helped to judge whether two polymers are miscible or not. In this work, DMA was applied to confirm the effect of A-OLLA on PLA. Figure 5 shows the relation between temperature and storage modulus ($E'$) including tan $\delta$ of PLA/A-OLLA blend. At higher temperature, $E'$ increased with
increasing A-OLLA content. In addition, the peak of tan δ which is the $T_g$ of the materials shifted toward lower temperature with increasing A-OLLA content. The results indicated that the compatibility between PLA and A-OLLA due to OLLA segments on A-OLLA chain.

3. 5. Thermal stability of PLA/A-OLLA blends

Figure 6 shows the thermal degradation curves of PLA/A-OLLA blends compared to neat PLA and A-OLLA. It can be seen in Figure 6 that thermal degradation of A-OLLA proceeded in two steps. The first step was initiated by degradation of OLLA chain and started at . The second step was initiated by degradation of acrylic chain.

In relation to the thermal stability of PLA/A-OLLA blends, due to the low thermal stability of A-OLLA, a decrease in thermal properties of the blends compared to the neat polymer is not surprising. In this result, the thermal stability of the blend (10 phr A-OLLA) at 5 wt% loss was decreased by 14 °C compare to neat PLA.
4. CONCLUSION

In this study, we synthesized successfully poly(butyl acrylate-co-hydroxyethyl methacrylate-g-lactide) (A-OLLA) graft copolymer by copolymerization of hydroxyethyl methacrylate terminated oligo(L-lactide) (HEMA-OLLA) and n-butyl acrylate (BA). Confirmation of the chemical structure and the molecular weight of the product was characterized using by $^1$H-NMR and GPC, respectively.

To study the effect of A-OLLA on the mechanical and thermal properties of PLA, blends of PLA and A-OLLA were prepared by melt blending. Addition of up to 10 phr A-OLLA into PLA led to a progressive decrease in the tensile stress, Young’s modulus and thermal stability. The highest impact performance was obtained by addition of 10 phr A-OLLA. As observed in the SEM images, the fractured surfaces of the blend samples with 5 or more A-OLLA were rough, which is indicative of the improved toughness.
5. REFERENCES


Table 1. Characteristics of HEMA-OLLA and A-OLLA as Determined by $^1$H-NMR and GPC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>DP(^a)</th>
<th>$M_n(^b)$ (g/mol)</th>
<th>$M_w(^b)$ (g/mol)</th>
<th>PDI (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA-OLLA</td>
<td>40.2</td>
<td>4,300</td>
<td>6,600</td>
<td>1.5</td>
</tr>
<tr>
<td>A-OLLA</td>
<td>40,000</td>
<td>109,000</td>
<td></td>
<td>2.56</td>
</tr>
</tbody>
</table>

\(^a\) DP (degree of polymerization) : ratio of integrals of methyl protons of lactide to methyl protons of HEMA, measured by $^1$H-NMR

\(^b\) Analyzed by gel permeation chromatography.
Table 2. Mechanical Properties of Neat PLA and PLA/A-OLLA Blends.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile stress (MPa)</th>
<th>Tensile modulus (MPa)</th>
<th>Impact strength (kgf-cm/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>55±0.4</td>
<td>1187±38.6</td>
<td>1.44±</td>
</tr>
<tr>
<td>Blend with 1 phr A-OLLA</td>
<td>53±0.72</td>
<td>1060±25.5</td>
<td>2.67±0.06</td>
</tr>
<tr>
<td>Blend with 3 phr A-OLLA</td>
<td>49±0.8</td>
<td>870±32</td>
<td>2.98±0.21</td>
</tr>
<tr>
<td>Blend with 5 phr A-OLLA</td>
<td>44±0.3</td>
<td>772.1±34.6</td>
<td>3.91±0.06</td>
</tr>
<tr>
<td>Blend with 10 phr A-OLLA</td>
<td>38±0.7</td>
<td>680±28</td>
<td>6.13±0.07</td>
</tr>
</tbody>
</table>
(a) Synthesis of HEMA-OLLA macromonomer

2-hydroxyethyl methacrylate (HEMA) + L-lactide (LA) $\xrightarrow{150^\circ C, 24\,h\quad \text{Sn(OEt)}_2}$ Hydroxyethyl methacrylate terminated poly(L-lactide) (HEMA-OLLA)

(b) Synthesis of A-OLLA

Hydroxyethyl methacrylate terminated poly(L-lactide) (HEMA-OLLA) + n-butyryl acrylate (BA) $\xrightarrow{80^\circ C, 1\,h\quad \text{AIBN}}$ Poly(butyl acrylate-co-hydroxyethyl methacrylate-g-lactide) (A-OLLA) graft copolymer

Figure 1. Reaction schemes for the synthesis of (a) HEMA-OLLA macromonomer and (b) A-OLLA.
Figure 2. $^1$H-NMR spectra of (a) HEMA-OLLA and (b) A-OLLA.
Figure 3. Mechanical properties of the PLA/A-OLLA blends: (a) tensile strength, (b) Young’s modulus and (c) impact strength.
Figure 4. SEM images of Izod-fractured surface of the PLA/A-OLLA blends: (a) neat PLA, (b) blend with 3 phr A-OLLA, (c) blend with 5 phr A-OLLA, and (d) blend with 10 phr A-OLLA.
Figure 5. Dynamic mechanical analysis of the PLA/A-OLLA blends.
Figure 6. Thermogravimetric analysis of the PLA/A-OLLA blends.