Biodegradable Polymer Blends of Poly(lactic acid) and Starch

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Abstract: Poly(lactic acid)(PLA) and starch were melt-blended using a twin screw mixer. To improve the toughness of blends, poly(e-caprolactone) (PCL) was added up to 30 wt%. Blends were characterized by DSC thermal analysis, tensile test, morphological analysis and ATR IR spectroscopic analysis. The addition of starch gave little influence on thermal properties. In particular, the starch content of 5 wt%, the crystallinity of PLA were the highest. The addition of starch resulted in reducing the tensile strength and elongation ratios. PCL was found to be effective in improving toughness. ATR IR spectra showed that the C=O band of PLA shifted when starch was added, indicating that some hydrogen bonding formed between the ester group of PLA and the hydroxyl group of starch. Morphological results by polarized optical microscopy showed that the size of the spherulite became smaller and less regular as the content of starch increased.

Introduction

Recently, much attention has been paid to degradable aliphatic polyesters because of their biodegradability and biocompatibility. Especially, industrial interest in poly(lactic acid) (PLA) is increasing not only for biomedical applications, but also for potential large scale uses such as packaging materials, food containers, coating materials and so on. These polymers are easily hydrolyzed in the presence of moisture, and their hydrolyzed products are nontoxic and harmless to human beings.1-3

There are four types of PLAs as there are two stereoisomeric forms of lactic acid. Poly( DL-lactic acid)(PDLLA) and poly( L-lactic acid)(PLLA) are the two stereoregular polymers. Poly( DL-lactic acid)(PDLLA) is a racemic polymer obtained from an equimolar mixture of D- and L-lactic acid, and meso-PLA can be obtained from D,L-lactide.4 Among them, PLLA possesses good mechanical properties and clarity besides its processability. But its brittleness is its major defect for many applications. Moreover, the relatively high price of the intermediate lacticide lowers the possibility of their commercialization. In order to modify various properties or to lower the price, studies on PLLA blends with other polymers have been carried out.5-10 PLLA was reported to be miscible with other stereoisomer such as PDLA. The blends of PLLA and PDLA exhibited a property change according to the mixing ratio.5,6 It is also known that PLLA is able to form miscible blends with various polymers such as poly(ethylene oxide),7 poly(vinyl acetate)8 and poly(ethylene glycol).9 Kricheldorf et al. carried out transesterification studies on blends of PLLA with poly(lactones).10

Blending starch and starch derivatives, both in granular and destructured forms, with various polymer has been investigated. For the sake of giving some biodegradable characteristics to the thermoplastic polymer, they have been blended with common plastics such as polyethylene,11 poly(vinyl chloride),12 poly(ethylene-co-vinyl alco-
Moreover, starch is also blended with other biodegradable polymers such as aliphatic polyesters as well as with non-biodegradable polymers in order to lower the cost of the finished product and enhance the biodegradability. The well-known examples are PCL/starch blend, poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/starch blend\(^\text{15}\) and poly(vinyl alcohol)/starch blend.\(^\text{16}\)

In this work, blends of PLLA and starch were prepared for the purpose of combining good mechanical properties of PLLA with the low cost of starch. The effects of adding starch on thermal/mechanical properties, morphology of the blends were investigated. Besides, in order to obtain less brittle blends, poly(e-caprolactone) (PCL) was also added.

**Experimental**

**Materials.** Star-shaped PLLA with six arms(S-PLA) and linear PLLA(L-PLA) used in this research were provided by Korea Institute of Science and Technology(KIST). The molecular weights of S-PLA and L-PLA were approximately 61,000 and 367,000, respectively. PLA was purified by reprecipitation using chloroform as the solvent and methanol as the precipitant. PCL was obtained from Union Carbide with number average molecular weight of 80,000. High amylose corn starch was purchased from Sigma Chemicals (grade : A-7043) with amylose content of 70%. PLA and PCL were dried under vacuum at 40°C for 24 h before use. Starch was also dried in a vacuum oven at 80°C for 24 h.

**Preparation of Samples.** All blends were prepared using a Haake RotorMix 600 at 180°C for L-PLA and at 160°C for S-PLA. The mixing time was 5 min. PLA/starch blendings were performed at the ratios of L-PLA(or S-PLA)/starch from 95/5 to 70/30 in 5 wt% intervals. In case of PLA/PCL/starch blends, the ratios of L-PLA(or S-PLA)/PCL were 90/10 and 70/30, and starch was added at the ratios of starch each PLA/PCL blend from 5/95 to 20/80 in 5 wt% intervals. After blending, all samples were cooled to room temperature. Films were prepared using a hot press at 185°C for mechanical testing of L-PLA blend and 165°C for S-PLA blend. The prepared films were quenched in cold water, and dried under vacuum at room temperature for 48 h, and stored in a desiccator with P2O5. Films of PLA/starch blends were prepared by the solution casting method using chloroform as a solvent. Blends were dried under air atmosphere at room temperature for 48 h and then were further dried under vacuum for 48 h.

**Thermal Analysis.** A Perkin Elmer DSC 7 was used to investigate the thermal behavior of the blends. All the blends from the mixer were dried in a vacuum oven at room temperature for 98 h in order to remove water thoroughly. The first scans were conducted at a heating rate of 10°C/min between 0°C and 200°C under a nitrogen atmosphere. Rapid cooling to 0°C allowed the samples to freeze in amorphous states. The transition temperatures determined from the second heating were reported.

**ATR IR Spectroscopy.** ATR IR spectroscopy was performed using a Mattson Alpha-Centauri FTIR spectrophotometer. The samples were heated to 185°C for the L-PLA blends and 165°C for the S-PLA blends on a slide glass until these polymers melted completely and formed thin films and then quenched to 0°C in cold water.

**Morphology.** The samples were heated to 185°C for the L-PLA blends and 165°C for the S-PLA blends on a slide glass until melted perfectly and formed a thin film, and then cooled to 110°C in an oil bath and kept at this temperature for 2 h. Optical microscopic examination was performed using a Nikon polarized light microscope (OPTIPOTO-POL). The samples were fractured in liquid nitrogen, then the fracture surfaces were observed using a SEM(Jeol JSM 35-CF, Japan).

**Tensile Properties.** The ultimate tensile strength (UTS) and the maximum elongation ratio were determined using an Instron testing machine (model 4465) at a crosshead speed of 10 mm/min. The samples were prepared in dog-bone shapes with a gauge length of 25 mm and a width of 5 mm. An average of five test values was taken for each sample.

**Results And Discussion**

**Thermal Properties.** Figure 1 shows DSC
polymers with the same molecular weight.\textsuperscript{17}

The melting peak of pure PCL is observed at 56°C (Figure 1(c)). The temperature of crystallization, $T_c$, of L-PLA/PCL blends (Figure 1(d)) shifted to a lower temperature and the width of crystallization peak became narrower than that of pure L-PLA. This result could be explained that PCL melts improved the mobility of L-PLA, that is, the PCL melts played a role as a plasticizer, and consequently the crystallization of L-PLA was accelerated.

In the case of S-PLA/PCL blends (Figure 1(e)), $T_m$ of PCL and $T_s$ of S-PLA overlapped at approximately 56°C in the DSC thermograms. $T_s$ is clearly observed at 112°C. The narrow width of the crystallization peak indicated that PCL melts played a role as a plasticizer in this blend as well. It was remarkable that a double endothermic peak was observed in the DSC thermogram of S-PLA/PCL blend. Double or multiple melting peaks have been reported for several polymers or polymer blends, and various theories exist about the origin of multiple melting. Bell and Dumbleton attributed the occurrence of double melting peaks to the presence of morphologically different crystal structures such as folded-chain crystals and crystals containing partially extended chains.\textsuperscript{18} On the other hand, Roberts explained the occurrence of double melting in terms of recrystallization during melting, and consequently formation of higher melting crystals.\textsuperscript{19}

In the case of PLA/PCL blend, a reliable theory has never been proposed. We thought that the double peaks appeared because S-PLA became more mobile as PCL melt and the enhanced mobility of S-PLA induced recrystallization during

![Figure 1. DSC curves of L-PLA(a), S-PLA(b), PCL(c), L-PLA/PCL(7/3)(d), and S-PLA/PCL(7/3)(e).](image)

<table>
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<tr>
<th>Starch Content (wt%)</th>
<th>$T_d$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_s$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_s$ (°C)</th>
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<tbody>
<tr>
<td></td>
<td>$\Delta H$ (J/g)</td>
<td>$\Delta H$ (J/g)</td>
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<tr>
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$\Delta H$ was calculated except starch content.
melting. But considering that the double melting peak was observed only from the blends containing S-PLA, we could also suppose that the star shaped structure or low molecular weight led to occurrence of double melting peaks. Consequently, we thought that double melting peaks of S-PLA blends was due to the complex effect of all factors as stated above.

The maximum peak temperatures (onset for $T_d$) and heat of fusion in DSC thermograms for PLA/starch blends are denoted in Table I. When starch was added, $T_d$'s of both L-PLA and S-PLA/starch blends remained almost unchanged, but crystallization characteristics were influenced. In the case of L-PLA/starch blends, the width of exothermic peaks for crystallization became narrower and maximum peak temperatures shifted to the lower temperatures. These results were indicative of an increase in the rate of crystallization. Besides, $\Delta H$ for crystallization and melting became larger as the content of starch increased. These results suggested that starch played a role as a nucleating agent. Both $T_c$ and $T_m$ were clearly observed in DSC thermograms of S-PLA/starch blends. $T_c$ and $T_m$ were the lowest at the starch content of 5 wt% and shifted to the higher temperature as the content of starch increased over 5 wt%. $\Delta H$ for crystallization and melting were the highest at the starch content of 5 wt% and decreased as the content of starch increased over 5 wt%. This tendency indicated that starch played a role as a nucleating agent enhancing crystallization of S-PLA. But the effect was declined when the content of starch was over 5 wt%. We thought that when starch content was high, starch aggregated and particle sizes of starch aggregation became larger, and consequently, these large starch particles prevented the growth of crystals. The overall influence of the starch addition on S-PLA was larger than that of L-PLA/starch blends. Especially, only S-PLA/starch blends showed a decrease of the influence with an increase of starch content.

Figure 2 shows DSC thermograms of ternary PLA/PCL/starch blends. When starch was added to L-PLA blends (Figure 2(a)), characteristic peaks did not change but the $T_c$ around 100°C shifted to a lower temperature by approximately 2°C as compared with that of binary PLA/PCL blends. This may be an evidence that starch played a role as a nucleating agent. When the content of starch increased, the characteristic peaks remained unchanged. In the case of S-PLA blends, the addition of starch resulted in lowering the $T_c$ by approximately 3°C. These results were the same as those from L-PLA blends.

**ATR-IR Analysis.** Figure 3 shows IR spectra of starch, S-PLA, L-PLA, and PCL. The spectrum of starch showed strong band at 1022 cm\(^{-1}\) which corresponded to C-O group, and broad bands in 1466-1450 cm\(^{-1}\) and 1375-1365 cm\(^{-1}\) regions which corresponded to the asymmetrical and symmetrical bands of C-H group. The spectra of S-PLA and L-PLA showed strong C=O and C-O bands of ester group at 1750 cm\(^{-1}\) and 1300-1000 cm\(^{-1}\) regions, respectively, and strong C-H stretching bands in the 2950-2800 cm\(^{-1}\) region. The C=O band of ester group in PCL appeared at 1725 cm\(^{-1}\) which was lower than the wave number of C=O bands in PLA.

Figure 4 shows IR spectra of PLA/starch and PLA/PCL blends. In the case of S-PLA/starch with starch content of 10 wt% (Figure 4(b)), the C=O
resulted in the increase of the crystallinity of S-PLA. When the content of starch was 20 wt% (Figure 4(a)), the shift was not observed. That is, the increase of the starch content over 10 wt% resulted in the decrease of the hydrogen bonding. These results corresponded with DSC results that $\Delta H$ of crystallization and melting for S-PLA/starch blends showed maximum values when the starch content was 5 wt% and decreased as the starch content was over 5 wt%.

In the case of PLA/PCL blends with the PCL content of 30 wt% (Figure 4(d) and (e)), the C=O band was shifted to lower wave numbers compared with those of pure PLA. In particular, the shifts for L-PLA blends (1733 cm$^{-1}$) were larger than those for S-PLA blends (1749 cm$^{-1}$), because the molecular chains of L-PLA were more easily accessible to PCL chains than those of S-PLA leading to enhanced hydrogen bonding. Figure 5 shows IR spectra of PLA/PCL/starch blends where the starch content was 5 wt%. The C=O band shifted to a lower wave number and the shift was very large. In the case of S-PLA blends, this result corresponded with DSC results that the degree of crystallinity was the highest at the starch content of 5 wt%.

**Morphology.** Polarized optical micrographs of the blends are shown in Figure 6. The spherulites of both L-PLA and S-PLA/starch blends had a
good fibril structure grown radially at 110°C (Figure 6(a) and (b)). The average radius of spherulites was about 140 μm for pure L-PLA and 120 μm for pure S-PLA. When the starch content increased, the sizes of the spherulite decreased and more irregular. These results indicated that starch played a role as a nucleating agent and the size and shape of the spherulites changed. When the starch content was 5 wt% in S-PLA/starch blends, the surface of the spherulite was rough compared with those of L-PLA/starch blends. When the content of starch was 20 wt%, the sizes of spherulites were very small and dispersion and size of spherulites were homogeneous.

Figure 7 shows SEM photographs of fracture surface of L-PLA/starch blends. Starch particles with the diameter of 5-7 μm were dispersed. When the starch content was 5 wt% (Figure 7(c) and (d)), it was observed that starch particles cling to the matrix. With the starch content of 20 wt%, the voids appeared, as a result of the separation of starch particles from the matrix. Particularly in the case of S-PLA/starch blends (Figure 7(h)), this separation was observed more easily and the size of the void was larger than that in L-PLA/starch blends. Also the aggregation of starch particles were observed. These results were due to the poorer interaction between starch and S-PLA than that between L-PLA and starch. We thought that the decrease of crystallinity with an increase of the starch content over 5 wt% in DSC results was owing to this morphological defect of S-PLA/starch blends.

Tensile Properties. According to Nielsen, on the assumption that the adhesion between a filler and matrix is perfect in the composite, the relationship between the elongation at break of the composite (ε) and volume fraction (φ) can be expressed by equation (1).

$$\varepsilon = \varepsilon_0 (1 - \phi)^{0.5}$$  \(1\)

where $\varepsilon_0$ is the elongation at break of the only matrix. If the adhesion between a filler and matrix is poor, the elongation at break will be decreased more gently with an increase of volume fraction of filler as compared with values calculated by equation (1).

On the other hand, the tensile strength of the composite can be represented by equation (2) on
the assumption that the adhesion between a filler and matrix do not exist at the least.

\[ \sigma = \sigma_0 (1 - 1.21 \phi^0.75) \]  

(2)

where \( \sigma_0 \) was the tensile strength of the only matrix and the constant of 1.21 is the 2/3th power of 0.75 which is the volume fraction of a sphere shaped filler when the fillers are filled perfectly with an arrangement of hexagon or face centered cubic.

Willett et al. have reported LDPE/granular starch composite using these equations. In this study, these equations were used, and the volume fraction of starch was determined by using the following equation.

\[ \phi = \frac{\rho_{\text{starch}}}{\rho_{\text{total}}} \]  

(3)

where \( \rho \) is the weight fraction and \( \rho \) is the density of starch, 1.4 g/cm³.

Because PLA/starch blends are very brittle, the film preparation using a hot press is very difficult. For that reason, the films of PLA/starch blends for the tensile test were prepared by the method of solution cast. But in the case of PLA/PCL/starch blends, testing samples could be prepared using a hot press because the addition of PCL increased the flexibility.

Figure 8 shows the relative tensile strength of PLA/starch blends versus the volume fraction of starch when the tensile strength of the only matrix is adopted as unit of height axis. The solid line is the prediction by equation (2), that is to say, the relative tensile strength versus the volume fraction of starch on the assumption that the adhesion between a filler and matrix do not exist at all. The dot line was the least squares fit obtained by averaging all the five sets of experimental data at each value of \( \phi \). For both L-PLA/starch and S-PLA/ starch, the slopes are gentler than that of the straight line. This result suggested that some adhesion existed between PLA and starch. It corresponded with ATR IR results, which were discussed above.

Especially L-PLA/starch blends showed lower slopes than those of S-PLA/starch blends. That is, an increase in volume fraction of starch had greater effects on the tensile strength of S-PLA/starch blends. This result was due to morphological defects of S-PLA/starch blends, which were discussed above.

Figure 9 shows the relative elongation of PLA/starch blends. The solid line shows the prediction by equation (1). In other words, the relative elongation at break versus the volume fraction of starch on the assumption that the perfect adhesion exists between a filler and matrix. There is a
Figure 10. Relative tensile strength of PLA/PCL/starch blends.

Figure 11. Relative elongation of PLA/PCL/starch blends.

wide difference between the dot lines and the solid line. This is due to the poor adhesion between PLA and starch.

The relative tensile strength and the relative elongation for PLA/PCL/starch blends are shown in Figure 10 and 11, respectively. These results are similar to those of PLA/starch blends. It was also found in PLA/PCL/starch blends that a certain adhesion exists between PLA and starch but the adhesion was poor. The mechanical properties of PLA/PCL/starch blends could not be com-

pared with those of PLA/starch blends because the methods of the sample preparation were different from each other. Therefore, the effect of PCL addition could not be determined. But considering that only testing samples of PLA/PCL/starch blends were prepared using a hot press, we thought that the addition of PCL enhanced the toughness of the blends.

Conclusion

1. Addition of starch lowered the temperature of crystallization and increased the degree of crystallinity in PLA/starch blend. That is, starch played a role as a nucleating agent. In the case of L-PLA blends, when the content of starch increased, this effect increased. But in case of S-PLA blends, this effect was maximal at the starch content of 5 wt%.

2. ATR IR spectra showed that starch addition resulted in a shift of C=O band of PLA. This shift suggested that some hydrogen bonding existed between the ester group of PLA and the hydroxyl group of starch.

3. The size and shape of the spherulite were dependent on the content of starch. When the content of starch increased, the size was smaller and less regular. The voids appeared, which were formed as the separation of starch particles from the matrix proceeded. In the case of S-PLA/starch blends, this separation was observed more easily and the void size was larger as compared with L-PLA/starch blend.

4. The relative mechanical properties showed that some adhesion existed between PLA and starch but the adhesion was poor. The addition of starch resulted in reducing the tensile strength and elongation of blends.

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