Properties and Biodegradability of Polylactide for Paper Coating Application

− Poly(ʟ−lactide) and Poly(ᴅ−lactide) Blend −

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ABSTRACT

Poly($_D$-lactide) ($_D$-PLA) was synthesized to have low molecular weight for miscible blends with a high molecular poly($_L$-lactide) ($_L$-PLA). The blends were prepared by dissolving the two components of $_L$-PLA and $_D$-PLA (w/w) in chloroform (100/0, 90/10, 70/30, 50/50, 30/70, 0/100). The miscibility of these miscible blends was characterized by gel-permeation chromatography (GPC), differential scanning calorimetry (DSC), and the selective degradability by enzymes (proteinase K, subtilisin and ɑ-chymotrypsin). The coating efficiency of PLA blends onto paper was determined and the degrading activity cellulases by on these blends. The miscibility, coating efficiency and enzymatic degradability of these blends were decreased according to increasing of $_D$-PLA blending part. Such results were attributed to the extent of coating application of PLA, with better miscibility (compatibility), coating efficiency and degradability due to a higher $_L$-PLA content.

1. Introduction

Conventional plastics such as polyethylene and polypropylene have accumulated as non-degradable solid wastes after disposal. Biodegradable plastics were developed to protect the environment from conventional plastic wastes. Several biodegradable plastics are now commercially available, including synthetic polyesters such poly($_L$-lactide) (PLA), poly(ε-caprolactone) (PCL) and poly(butylene succinate) (PBS), and microbial polyesters including poly(β-hydroxyalkano-ates) (PHA) such poly(β -hydroxybutyrate)

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(PHB) (1-5). Applications of biode gradable plastics are emerging fast and expected to grow rapidly, particularly for one-trip and technical packaging, paper and board coating, adhesives, paints, agricultural and horticultural applications (4,6). The pulp and paper industry has also been the target of environmental groups all over the world (7).

Polylactide (PLA) has been one of the most widely studied biodegradable polymers because of its excellent optical and mechanical properties (4, 8-9). PLA is made by fermentation of starch from agricultural products like potato or corn (can be obtained from wet milling of corn, or from food wastes). PLA is crystalline and strong (hardness similar to acrylic plastic), and the costs of production are now reducing (10-12). Conn et $al.$ (12) firstly reported that the uses of PLA considered as part of this safety assessment involve applications such as disposable cutlery, cups, plates, straws, stirrers, lids, certain packaging applications, and cups, plates and containers for foods dispensed at delicatessens and fast-food establishments.

The most common polylactides (PLAs) are L-PLA and poly(D-lactide) (D-PLA), which are produced from L-lactide and D-lactide, respectively. L-PLA is a semicrystal-line polyester with a melting temperature (T_m) of 180 °C (13). To meet various mechanical and degradation requirements, PLA must exhibit a broad spectrum of physical properties while retaining the degradability of the parent poymer (14). There are several approaches for improving the properties of PLA, including bending and copoymerization (15). In recent years, there has been a growing interest in blending PLA with other polymers because blending is relatively simple and more cost-effective in comparison with copolymer

synthesis to modify polymer properties, and it can represent, in some cases, an alternative to copolymerization (11,15-16). Generally, blends exhibit advantageous physical and chemical properties that each individual polymer does not possess. Because a polymer-polymer complex can be formed upon mixing two polymers with different chemical compositions if a favorable interaction prevails between the different polymer chains as with complementary nucleic acids and proteins (17). Properties of blends depend not only on the compatibility or miscibility of the components; however, most of the blends are immiscible. Extensive effort is necessary to the study of the effect of blending and copolymerization of PLA on the physical and chemical properties of the final products.

In this study, the solution blends of both L-PLA and D-PLA with low molecular were investigated the miscibility, coating efficiency and enzymatic degradability of PLA blends by coating them onto paper for use in packaging and other applications. Also, thermal properties and morphology on paper of blends were also characterized. It is expected that blending of L-PLA and D-PLA may be an effective method for obtaining PLA-based materials.

2. Experimental

2.1 Materials

L-PLA, LACTY 1012 (number-average molecular weight, Mn = 3.4 x 10^5), was obtained from Shimadzu Co. Ltd., Japan. The D-PLA sample used in this study was synthesized in our laboratory according to ring-opening polymerization of D-lactide in the presence of 0.05% stannous octanoate (i.e. stannous 2-ethylhexanoate) as a catalyst. It was
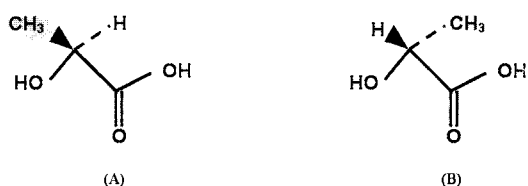
Fig. 1. Chemical structure of ʟ-lactic acid and ᴅ-lactic acid unit, a monomer unit of ʟ-PLA (A) and ᴅ-PLA (B).

performed at 130 °C under nitrogen for 2 h after recrystalization of lactides by 1 time dry ethyl acetate. The chemical structure of ʟ-lactic acid and ᴅ-lactic acid unit, a monomer unit of ʟ-PLA and ᴅ-PLA are compared in Figure 1. The paper used was No. 2 filter paper from Advantec Toyo.

The following 3 enzymes were used for blends degradation: proteinase K (chromatographically purified, ICN Biomedicals Inc.), subtilisin, α-chymotrypsin (three times crystallized from four times crystallized chymotrypsinogen) (Sigma Chemical Co.). Each enzyme was dissolved in a 0.1M phosphate buffer (pH 7.0), and used for following experiments after appropriate dilution.

Trichoderma reesei, Trichoderma viride and *Trichoderma viride* Onozuka cellulases were purchased from Sigma Chemical Co. (USA), Wako Pure Chemical Industries Ltd. (Japan), and Yakult Honsha Co. (Japan), respectively.

2.2 Preparation of ʟ–PLA/ᴅ–PLA solution blends powder

Solution blending was used in this study. All the blends were prepared by mixing different percentages (100/0, 90/10, 70/30, 50/50, 30/70 and 0/100, respectively) of a 1 % (w/v) of the two components (ʟ-PLA and ᴅ-PLA) in chloroform solution. The solvent was mixed to

miscibility for 6 h. ʟ–PLA and ᴅ–PLA blending solutions were made into powder for measuring their characteristics. Blends powder was prepared by addition of 500 ml methanol and homogenization at 10,000 rpm for 10 min using a homogenizer (Nissei AM-9, Japan), with no addition of surfactant. The blends powder in chloroform/methanol solution was filtered and air-dried for 1 d. The powder was then sieved through a 250 μm wire screen before use.

2.3 Preparation of PLA blends coated paper

Blends powder in chloroform were prepared at a concentration of 1% (w/v) and then prepared by penetration of PLA blends onto paper. Pieces of paper No. 2 (Advantec Toyo; 10 x 10 mm, 12 mg, thickness ca. 240 μm) were immersed one at a time in a PLA blends solution for 10 s, air-dried for 30 s, and dried at 30 °C in a vacuum oven for 1 d. Each piece of the paper was coated with approximately 0.6 mg of PLA (thickness ca. 245 μm). The PLA coated papers obtained were thicker than the paper by ca. 5 μm. For enzymatic degradation, 8pieces of coated paper containing about 5 mg PLA were used as substrates.

2.4 Gel permeation chromatography

The molecular weight of the blends powder (2 mg film/2 ml chloroform) was measured at 40 °C by a Tosoh GPC system (HLC-8120 GPC, refractive index monitor: RI-8020, Japan) with TSK Gel Columns (GMH$_{XL}$ X 2) using polystyrene as a standard. Chloroform was used as mobile phase (flow rate 0.8 ml/min).

2.5 Thermal analysis

The melting point (10 mg film sample) was measured with DSC, A SSC/5200 Seiko Instruments Inc. DSC (Japan). The samples were heated from 0°C to 240°C at the heating

rate of 10 °C/min under liquid nitrogen. The glass-transition temperature (T_g) was taken as the temperature at the mid point of the corresponding heat-capacity jump in the heating runs. The melting temperature (T_m) was determined from the maximum and the area of the melting endothermic peaks. DSC studies revealed the significant thermal properties of the samples, such as transition temperature (T_g) and melting temperature (T_m).

2.6 Coating efficiency of PLA blends onto paper

The coating efficiency of PLA blends onto paper was determined from decline in activity of cellulase. PLA coated papers were prepared as mentioned above for measuring cellulase activity. Cellulase degradation of the PLA coated papers and paper was carried at 37 °C, 14 h. The coating efficiency index of PLA onto paper was calculated as follows:

$$1 - \frac{Degradation \ of \ coated \ paper}{Degradation \ of \ paper \ (control)}$$
$$= Coating \ efficiency \ index \ [1]$$

2.7 Scanning electron microscopy

The surface structure of the PLA coated paper was observed under a JEOL scanning electron microscope (SEM), Model JSM-5310, operating at 15 kV acceleration. The sample was coated with gold using a JEOL, JFC-1200 fine coater before observation.

2.8 Enzymatic degradation

PLA coated papers were used as substrate for studying the PLA-degrading activity of enzymes. Enzymatic degradation was carried out in a 50 ml-vial using 5 mg substrate suspended in 3 ml of 0.1 M sodium phosphate buffer (pH 7) containing 1 ml of 0.05 % (w/v) octyl-glucopyranoside and 1 ml enzyme solution (1 mg/ml). The enzyme solution was prepared in 0.1 M sodium phosphate buffer (pH 7). In the substrate and the enzyme controls, the enzyme and the substrate were omitted from the mixture, respectively. The reaction mixture was incubated on a rotary shaker (100 rpm) at 37 °C for 14 h. After incubation, the solution was filtered through a 0.20 μm filter membrane for the measurement of water-soluble total organic carbon (TOC) concentration with a TOC-5000A analyzer (Shimadzu Co. Ltd., Japan). The TOC value was obtained after subtraction both controls from sample. TOC analysis is a simple assay of water-soluble substances of degradation products of PLA (monomer and oligomers) formed in the enzymatic reaction mixture.

3. Results and Discussion

3.1 Properties of L-PLA/D-PLA blends

Polymer blends prepared by different methods will have different thermal behavior. In this work, blends prepared by solution are discussed. The weight-averaged molecular weights are shown Table 1. The weight-averaged molecular weights of L-PLA, 90/10, 70/30, 50/50, 30/70, D-PLA were 40,500, 78,500, 91,500, 134,000, 169,000 and 1,760, respectively. From these data, it is clear that molecular weights of blends were increased by blending. The M_w/M_n ratio for L-PLA and D-PLA was decreased with increase in the concentration of D-PLA, which demonstrates the homogeneity in molecular weight.

One of the most common methods used to analyze stereocomplexes was DSC. Therefore, DSC was determined on L-PLA/D-PLA blends

Table 1. Characteristics of L-PLA/D-PLA solution blends powder

| L-PLA/D-PLA	Molecular weight $(M_n)^{a)}$	Polydispersity $(M_w/M_n)^{a)}$	T_g (°C)[b)]	T_m (°C)[b)]
100/0	40,500	5.5	60	165
90/10	78,500	3.4	60	164
70/30	91,500	2.8	61	192
50/50	134,000	2.4	63	199
30/70	169,000	2.1	63	197
0/100	1,760	1.7	–	140

a) The molecular weight of the polymer was estimated by gel-permeation chromatography
b) The galss transition temperature and melting temperature of the polymer was estimated by differential scanning calorimeter

to study the miscibility of the two polymers. Fig. 2 illustrates the thermograms obtained in the DSC heating run for L-PLA /D-PLA solution blends powder with different compositions range of 100/0 to 0/100. The T_g of a polymer blend is one of the most important criteria for indicating the miscibility of components. Miscibility between any two polymers in the amorphous state is detected by the presence of a single T_g intermediate between those of the two component polymers. Immiscibility of two polymers is demonstrated by the retention of T_g values of both individual components. On the basis of the DSC results, in solution blends, the T_g values of the L-PLA-rich phase increase slowly with an increasing D-PLA content in the blends, suggesting the presence of D-PLA in the L-PLA phase. The blend with a higher D-PLA content does not indicate a lower T_g value as compared with those of lower D-PLA content blends. Its lowest value seems to exist when the D-PLA content is 10% in the blend. Only one T_g was found in the L-PLA/D-PLA solution blends, indicating miscibility in this system.

T_m of the crystalline component in a polymer blend depends on both morphological and thermodynamic factors. Because all the blends are prepared under the same conditions in this

study, the T_m changes of the components depending on the composition could be due to specific interactions between the components. As shown in Table 1 and Fig. 2, the T_m values of blends are changed when the D-PLA content increases from 30 to 70%. A slight decrease in T_m was detected only when the content of L-PLA was 90%. This small T_m depression was due to the reduction of the crystallite size of L-PLA in the blends. From the DSC data, the T_g and T_m of blends changed significantly. It means that the solution blend was formed completely. On the other hand, the T_m and T_g of 90/10 L-PLA/D-PLA blend did not changed significantly.
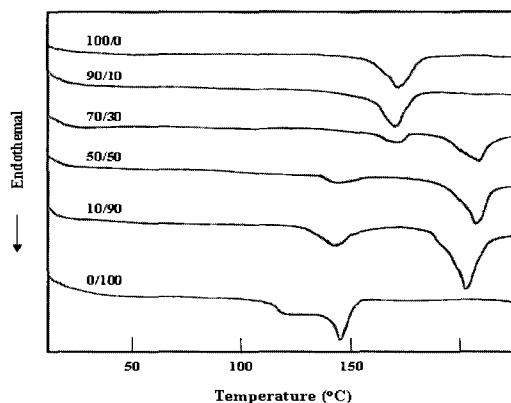
Fig. 2. DSC thermograms of L-PLA/D-PLA solution blends powder with compositions from 100/0 to 0/100.

3.2 Coating efficiency of the PLA blends onto paper

Coating efficiency of PLA onto paper depends on morphological factors of PLA. Paper is formed by a large number of cellulose fibers. The paper used in this study was a high quality filtration material made from 100% cellulose fibers. This paper has high coating efficiency and rapid penetration rate than ordinary commercial paper because it does not contain additives or some impurities. It is known that cellulose is degraded by various cellulases including cellulase of white-rot fungi, *Trichoderma ressei and Trichoderma viride*.(18) For the PLA coated papers, these enzymes preferentially degraded cellulose at the points of uncoated fibers. However, these cellulases did not degrade L-PLA and D-PLA powder. Hence, the coating efficiency the PLA onto paper could be determined from decline in the activity of cellulase.

Degradation of PLA blends coated papers and paper (control) was observed at 14 h of the reaction time (Table 2). All PLA blends coated papers showed lower cellulose degradation than that of cellulose paper. Among the coated papers, L-PLA coated paper exhibited the lowest biodegradability by cellulase. This confirmed the high coating efficiency of L-PLA onto the cellulose paper. In contrast, D-PLA coated paper showed the highest biodegradability by cellulase indicating the low coating efficiency of D-PLA into the cellulose paper. The coating efficiency index of blends coated paper decreased in the following order: L-PLA>90/10 > 70/30 > 50/50> 30/70>D-PLA.

Figure 3 shows SEM photographs of the L-PLA coated papers (B) (scale bar = 50 μm). In the case of L-PLA coated, SEM revealed that L-PLA was spread onto the surface of papers. Figure 4 illustrates the different model structures of the PLA blends coated papers prepared by penetration. By penetration, PLA

Table 2. Degradation of L-PLA/D-PLA solution blends coated paper by cellulases[a]

Solution blends coated paper (L-PLA/D-PLA)	TOC[b] (mg l^{-1})			Coating efficiency Index[f]
	Trichoderma reesei[c]	*Trichoderma viride*[d]	*Trichoderma viride Onozuka*[e]	
Paper (control)	310	130	270	0
100/0	133	51	167	0.5
90/10	182	46	151	0.5
70/30	205	59	172	0.4
50/50	245	69	198	0.2
100/0	133	51	167	0.5
90/10	182	46	151	0.5
70/30	205	59	172	0.4
50/50	245	69	198	0.2
0/100	287	89	261	0.1

a)The reaction mixture was composed of 5 mg as plasticin coated paper, 3 ml 0.1 M phosphate buffer (pH 7), 1 ml 0.05% (w/v) octyl glucopyranoside, and 1 ml enzyme (1 mg/ml).
b) Water-soluble total organic carbon
c) Sigma Chemical Co. (USA)
d) Wako Pure Chemical Industries Ltd. (Japan)
e) Yakult Honsha Co. (Japan)
f) Calculation by equation of (1)

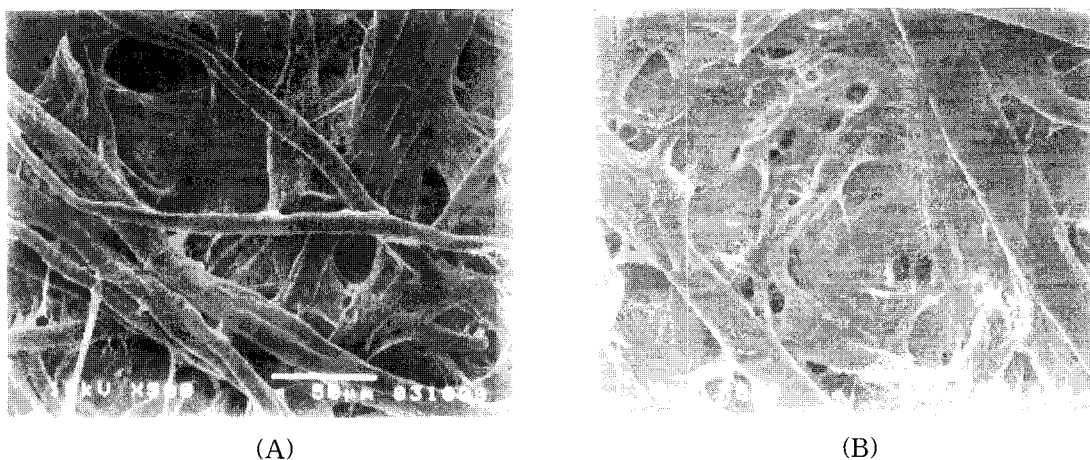(A)   (B)

Fig. 3. SEM photographs of the base paper (A) and the L-PLA coated papers prepared by penetration (B). Scale bar = 50 μm.

blends solution was penetrated onto the paper and then coated to cellulose fibers. Thus from our results, it can be considered that the coating efficiency of PLA blends is influenced by their phase morphologies.

3.3 Enzymatic degradability of the PLA blends

Two miscible binary blends, L-PLA/D-PLA were prepared by the coated paper from mixed blends powder solutions of chloroform and PLA degradability was measured by PLA-degrading enzymes, i.e., proteinase K, subtilisin and α-chymotrypsin. Recently, PLA, poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS) and poly(β-hydroxybutyrate) (PHB) coated papers were successfully utilized to enhance the interfacial penetration of cellulose

fibers (5). It can be used to improve the biodegradable polymer coatings, and attributed to packaging filed. Also, PLA-degrading enzymes may be useful for decomposition of the PLA blend plastics and it may extend the application fields of this plastic. Table 3 shows the TOC released after 14 h of enzyme reaction. The TOC value can be used as an index of the content of water-soluble PLA-oligomers and monomer formed by the hydrolysis and then released from the coated paper into the reaction mixture. The increase in D-PLA also means the decrease in the absolute quantity of L-PLA in the blend. Proteinase K showed the highest degradability followed by subtilisin and α-chymotrypsin. A decrease in TOC was observed when D-PLA was increased in blend. Furthermore, by calculating from the TOC

(A)   (B)   (C)   (D)   (E)   (F)
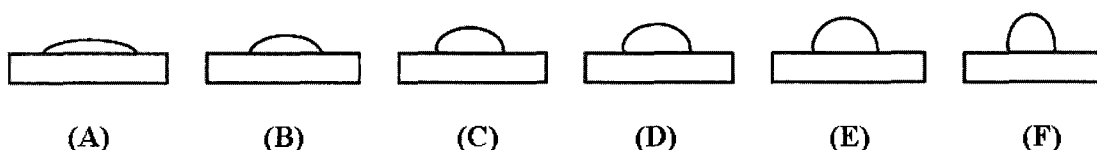
Fig. 4. Coating morphology of L-PLA/D-PLA blends into cellulose paper. (A) L-PLA, (B) 90/10, (C) 70/30, (D) 50/50, (E) 30/70, (F) D-PLA.

Table 3. Degradability of L-PLA/D-PLA solution blends by enzymes[a]

Composition (w/w) of L-PLA/D-PLA	TOC[b] (mg l^{-1})			Degradation of L-PLA(%)	Miscibility[c]
	Proteinase K from *Tritirachium album*	Subtilisin from *Bacillus licheniformis*	α-Chymotrypsin from Bovine pancreas		
100/0	283	257	209	100	–
90/10	274	241	182	90	100
70/30	74	44	31	19	27
50/50	13	7	7	3	6
30/70	1	0	11	2	5
0/100	26	0	2	0	–

a) The reaction mixture was composed of 5 mg as plastic in coated paper, 3 ml 0.1 M phosphate buffer (pH 7), 1 ml 0.05% (w/v) octyl glucopyranoside, and 1 ml enzyme (1 mg/ml). In cellulose paper control (without coating), no significant increase in TOC was observed.
b) Water-soluble total organic carbon
c) (TOC of blend/TOC of L-PLA)×100

produced by complete degradation of PLA blends, we confirmed that the percentage miscibility of blends decreased linearly with the increase in D-PLA content. In the blends containing 10% D-PLA showed the most miscibility.

4. Conclusions

PLAs and their copolymers have a specialty chemical, which could become one of the new sources of a family of environmentally friendly, compostable, and renewable polymers for use in packaging and other applications.

PLA blend from solution of both enantiomers (L- and D-)in chloroform was made at room temperature at a very slow rate. As the ratio of L-PLA and D-PLA, the solution blends were formed completely. However, in case of the miscibility by degradability after coating onto paper, L-PLA was found to show good miscibility with D-PLA at 90/10 ratio (w/w). L-PLA coated paper showed the lowest biodegradability by cellulase indicating the high coating efficiency of L-PLA onto the paper. On

the other hand, the degradability of L-PLA is better than that of D-PLA and the crystallization of L-PLA is weaker than that of D-PLA. Therefore, the morphology of L-PLA was suitable for coated paper.

The increasing use of biodegradable polymers like PLA has promoted intensive research into new material with potentional applications in every field.

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