

Preparation and Characterization of Starch/Polycaprolactone Blend

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ABSTRACT: To make starch/polycaprolactone (PCL) blend with high miscibility, starch was chlorinated (starch-Cl) by using methanesulfonylchloride ($\text{CH}_3\text{SO}_2\text{Cl}$) in dimethylformamide (DMF) prior to blending. Starch-Cl/PCL blends were prepared by the mixing between starch-Cl and PCL solutions under various conditions. To study the change of structure, thermal and physical characteristics of starch-Cl/PCL blend, FTIR, DSC, SEM, and solvent resis-

tance were measured. By blending starch-Cl and PCL, a chemical reaction occurred partially in blend (FTIR result); thereby, the miscibility (DSC and SEM results) and solvent resistance were increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1716–1723, 2004

Key words: starch-Cl/PCL blend; miscibility; FTIR; DSC; morphology

INTRODUCTION

Recently, much attention has been focused on the filling up of landfills by nondegradable plastic materials. The large volumes of plastics used to a large extent in packaging for fast food industry and in agricultural film became an issue of public attention on a potentially huge environmental accumulation and pollution problem. Their lack of degradability impacts significantly on the rate of depletion of landfill sites and their contamination of water or land surface. Recent trends in solid waste management and interest in biodegradable products have an effect on the policy to develop environmental friendly materials.^{1,2}

This led to legislation mandating recycling or development and use of alternative degradable materials. Despite this interest and research, production and consumption of nondegradable plastics increase by 5–10% every year. In this respect, biodegradable polyesters produced by organic synthesis or bacteria such as polycaprolactone (PCL), polyhydroxybutyrate (PHB), and polyhydroxyvalerate (PHV) are of considerable technological importance for use as commodity plastics as well as special polymers in medical applications.³ These biosynthetic polyesters are presently expensive to produce, however, and thus, it is unlikely that they will replace conventional thermoplastics in

applications where large quantities of materials are deployed.⁴

On the other hand, one of the natural biodegradable polymers, starch, is produced at a relatively low price.⁵ This natural polymer is currently used as a raw material or an ingredient in degradable or disposable plastic products.^{6,7} Well-known products made of starch, which are already established on the market, are agricultural foils, garbage or composting bags with a wide range of applications for short-time uses in the packaging or fast food industry.⁸

However, starch by itself exhibits poor physical and mechanical properties impossible to replace for nondegradable plastics used in commodity. To improve these physical and mechanical properties for starch, blending with hydrophobic and high-functional polymers is necessary.

Despite a variety of approaches that have been made,^{9–15} the improvements in physical and mechanical performance were little accomplished in starch/polymer blend systems. In these blended systems, two major common drawbacks have been point out: the incompatibility between starch and synthetic polymers, and the reduction of biodegradability of starch by the synthetic polymer.

An attractive way to increase the physical and mechanical performances in a starch-based blend system was to use material having miscibility and degradability as a reinforcing agent. Among many candidate materials, PCL was chosen more often because it has good mechanical properties and compatibility with many types of synthetic polymers.¹⁶ Hence, much research has been carried out to prepare completely

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biodegradable starch/PCL blends under various conditions.^{17–20} However, these studies showed that the physical and mechanical properties of the starch/PCL blends generally become poor with increasing starch content in the blend. This can be attributed to the incompatibility between the hydrophilic starch and hydrophobic PCL. Thus, it is expected that the properties of the starch/PCL blend could be improved by the chemical reaction, which can induce the enhancement of interfacial adhesion between starch and PCL phases.

Therefore, in this study, we try to prepare the starch/PCL blend with high miscibility. To enhance the interfacial adhesion between starch and PCL by chemical reaction under simple condition, first, starch was chlorinated; then, it was blended with PCL in solution state under various conditions. Finally, change of structure, thermal, morphologic characteristics, and solvent resistance were investigated.

EXPERIMENTAL

Materials and reagents

Cornstarch was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). PCL [molar mass: 10,000 (g/mol)] was kindly supplied by Daicel Chemical Ind. Ltd. (Osaka, Japan). Dimethylsulfoxide (DMSO), lithium chloride (LiCl), and methanesulfonylchloride ($\text{CH}_3\text{SO}_2\text{Cl}$) were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Dimethylformamide (DMF) and dimethylacetamide (DMAc) were purchased from Wako Pure Chemicals Ind. Ltd. (Osaka, Japan). All other chemicals were reagent grade and used without further purification.

Measurement of hydroxyl value

The hydroxyl value in PCL was measured by referring to the previous article.²¹ PCL (3 g) and acetic anhydride/pyridine solution (5% w/w, 200 mL) were mixed and reacted at 100°C for 3 h under N_2 . After being cooled to room temperature, it was titrated with 0.2N NaOH solution until neutralization. The hydroxyl value was calculated by

$$\text{Hydroxyl value (mol/g)} = [(A - B) \times N]/W \quad (1)$$

where A is the titration volume (mL) of the NaOH solution for blank; B is the titration volume (mL) of the NaOH solution for PCL; N is the normality of the NaOH solution; and W is the dry weight (g) of PCL.

Preparation of chlorinated starch

The starch was chlorinated as follows by referring to the previous article.²¹ Starch (15 g) and DMF (150 mL) were mixed in a four-necked flask equipped with a

mechanical stirrer, reflux condenser, thermocontroller, and N_2 inlet. Methanesulfonylchloride ($\text{CH}_3\text{SO}_2\text{Cl}$, 40–100 mL) was slowly added into the reaction mixture, and the reaction mixture was continuously stirred for 10 min to 24 h at 60 and 90°C, respectively. The reacted starch was precipitated by adding excess acetone (500–1000 mL) and then collected by vacuum filtration. The residue was washed several times with acetone and then dried in a vacuum oven (40°C) overnight.

Preparation of starch-Cl/PCL blend

Starch-Cl/PCL blends were prepared by following the two methods referred to in the previous article.²¹

Blend I type: Using DMSO

Starch-Cl (1 g) and DMSO (20 mL) were charged into the flask, equipped with mechanical stirrer, and then stirred over 10 min to dissolve well. Separately, PCL/DMSO solution (2 g/20 mL), which had been prepared through stirring at 70°C for 1 h to dissolve well, was mixed with starch-Cl solution. Stirring was continued for 30 min while maintaining the temperature at 70°C. After mixing for 30 min, the mixture was added to excess distilled water to remove unblended starch-Cl in starch/PCL blend system. The precipitated material was filtered off and washed several times over with distilled water. Finally, the starch-Cl/PCL blend was obtained by drying in a vacuum oven at 40°C for 24 h.

Blend II type: Using DMAc and LiCl

For preparation of blend II types, 1N LiCl-DMAc solution was used instead of DMSO; other conditions were same as used for the preparation of blend I type.

Structural characterization

Fourier transform infrared (FTIR) spectra were obtained from KBr pellets of the starch, starch-Cl, PCL, and starch-Cl/PCL blends with a FTIR spectrometer (Nicolet-360, Madison, WI, USA)

Thermal characterization

Thermal characteristics of the starch, starch-Cl, PCL, starch/PCL mixture, and starch-Cl/PCL blends were measured by using a differential scanning calorimeter (DSC) (MAC 3100s, Osaka, Japan) in a temperature range of $-50\sim 300^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.



Scheme 1 Preparation of starch-Cl.

Morphologic characterization

The morphology of starch-Cl/PCL blend was investigated by using a scanning electron microscope (SEM; JEOL, JSM-5200, Osaka, Japan). The samples were coated with gold/palladium on an ion sputter coater and observed by using 7 kV secondary electrons.

Solvent resistance

Starch, PCL, and starch-Cl/PCL blends (0.1 g) were dispersed in various solvents (25 mL); the dispersion was then vigorously stirred at 30°C for 24 h. The solvents tested included DMSO, distilled water, 0.5N NaOH, and HCl solution. The undissolved residue was filtered and then dried in a vacuum oven for weight measurement. The solvent resistance was calculated by:

$$\text{Solvent resistance} = \frac{\text{dry weight of residue}}{\text{after filtration/dry weight of initial sample}} \quad (2)$$

RESULTS AND DISCUSSION

Measurement of hydroxyl value

To check the existence of hydroxyl group in PCL with a molar mass of 10,000 (g/mol) prior to the preparation of starch-Cl/PCL blend, the hydroxyl value of PCL was measured by titration method. The hydroxyl value of PCL was about 0.23 mmol/g, showing a similar theoretical value.

Preparation of starch-Cl

The chlorination reaction of starch is briefly shown in Scheme I, and the color and degree of substitution

(DS) of chlorinated starches (starch-Cl) under various reaction conditions are shown in Table I. As shown in Table I, when cornstarch was chlorinated under lower reaction temperature (60°C), DS of starch-Cl was relatively small even though the reaction was carried out by using large volumes of methanesulfonylchloride (100 mL) for a long time (24 h). However, at higher temperature (90°C), sufficient temperature to be gelatinized for starch, DS increased largely even though reaction was carried out by using small volumes of methanesulfonylchloride (40 mL) for a short time (1 h). Also, for higher temperature (90°C), increased reaction time (1 to 2 h) did not affect significantly on DS of starch-Cl. In the case of using 100 mL of chlorination agent ($\text{CH}_3\text{SO}_2\text{Cl}$), 31.1 g of chlorides were contained. This amount was much higher than that of the starch (15 g) used for the reaction. At lower temperature (60°C), the chlorination efficiency based on the reaction yield was low under the experimental conditions. However, at higher temperature (90°C), reaction efficiency was significantly increased. In our experiment, chlorination of starch was more affected by reaction temperature rather than amount of chlorination agent. This supported the following results. At lower temperature (60°C), the starch was not gelatinized then and was difficult to be chlorinated even though large volumes of chlorination agent (100 mL) were participated in chlorination reaction for long times. However, at higher temperature (90°C), the starch was gelatinized fully, which made it easy to be chlorinated with small volumes of chlorination agent (40 mL).

To check the introduced chloride onto starch, FTIR spectra of starch and starch-Cl (sample No. I-3) were measured and the results were then given in Figure 1. The native starch showed a typical broad peak for the hydroxyl groups at approximately 3400 cm^{-1} (marked by an arrow in Fig. 1). Identically shown in previous results²¹ by chlorination, FTIR spectra showed a new broad peak around 600 cm^{-1} on the spectrum, which was presumably attributed to the chloride attached to the C-6 methyl group of the anhydrous glucose units of starch, as well as the hydroxyl peak around 3400 cm^{-1} was substantially decreased, indicating the pres-

TABLE I
The Color and Degree of Substitution (DS) of Starch-Cl with Various Reaction Conditions

Sample No.	Reactants			Condition			DS ^a
	Starch solution		MeSO ₂ Cl (mL)	Temp (°C)	Time	Color	
	Starch	DMF					
I-1			100	60	24 h	Light brown	0.36
I-2			100	90	1 h	Dense brown	0.96
I-3	15 g	150 mL	50	90	10 min	Gray	0.26
I-4			40	90	1 h	Brown	0.83
I-5			40	90	2 h	Brown	0.86

^a Calculated by elementary analysis.

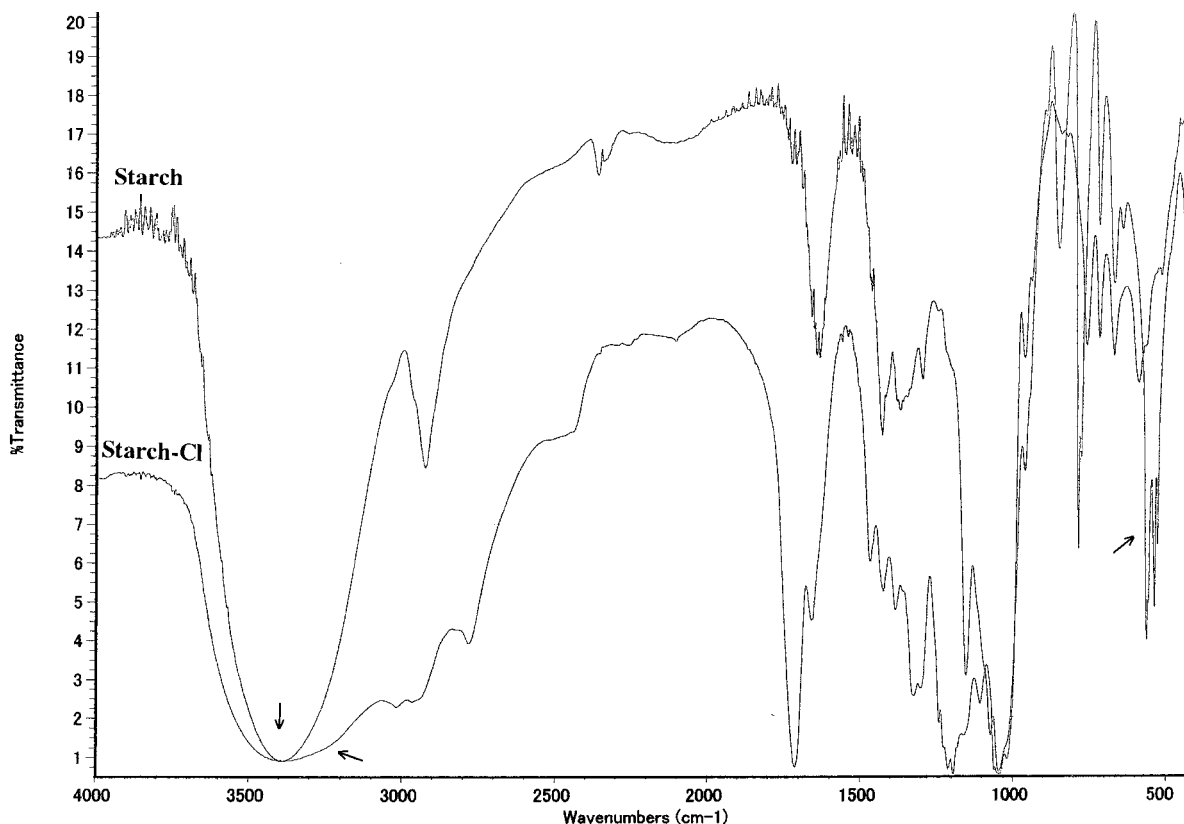


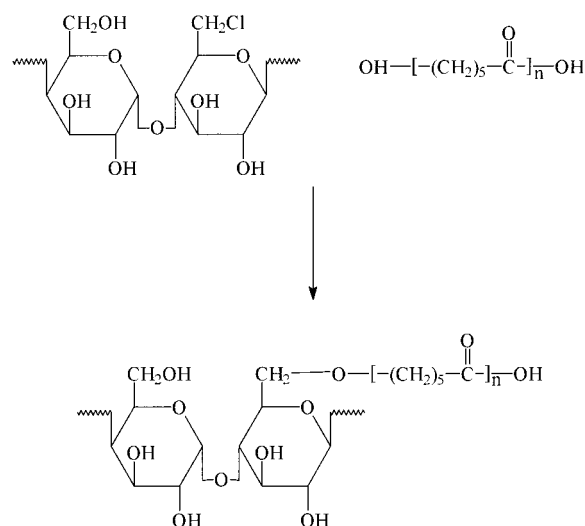
Figure 1 FTIR spectra of starch and starch-Cl.

ence of the substitution on the hydroxyl groups. These peak changes became more prominent in FTIR spectra with increasing DS of starch-Cl (data not shown).

Preparation of starch-Cl/PCL blend

When starch-Cl/PCL blend was prepared, the chemical reaction supposed to occur partially in starch-Cl/PCL blend system is shown briefly in Scheme II. Also, the color and yield of starch-Cl/PCL blend under various blending conditions are shown in Table II. In this experiment, the weight ratio of blend (starch-Cl/PCL) was used to fix one-half by referring to the previous article.²² As shown in Table II, in the case of using cornstarch, the yield of blend (sample No. II-3) was about 62%. This corresponds to any reaction that did not occurred between starch and PCL under our blending conditions. This also confirmed that FTIR spectrum of sample No. II-3 showed identically to that of pure PCL (data not shown). The production yield, calculated from the weight ratio between the final product (starch-Cl/PCL blend) and initial reactants (starch-Cl and PCL), was changed according to reaction conditions. When starch-Cl with higher DS was used in starch-Cl/PCL blend, the yield was increased consequently. Also, when DMSO was used as the solvent, the yields of starch-Cl/PCL blends were only

65~74%. However, when DMAc and LiCl were used, the yield was higher (69~80%) than that obtained in DMSO. This result supported the finding that the chemical reaction between starch-Cl and PCL was effective in LiCl-DMAc solution as mentioned in previous articles.²¹



Scheme 2 Chemical bond supposed to occur partially in starch-Cl/PCL blend.

TABLE II
The Color and Yield of Starch-Cl/PCL Blend with Various Conditions^a

Sample No.	Composition (g)					PCL	Solvent	Color	Yield ^b (%)
	Starch	Starch-Cl							
		I-1	I-2	I-3	I-4				
II-1	1	—	—	—	—	—		—	—
II-2	—	—	—	—	—	2		White	97
II-3	1	—	—	—	—	2		White	62
II-4	—	1	—	—	—	2	DMSO	Yellow	67
II-5	—	—	1	—	—	2		LB ^c	74
II-6	—	—	—	1	—	2		Yellow	65
II-7	—	—	—	—	1	2		LB	73
II-8	—	1	—	—	—	2		Yellow	69
II-9	—	—	1	—	—	2		LB	80
II-10	—	—	—	1	—	2	DMAc+LiCl	Yellow	69
II-11	—	—	—	—	1	2		LB	78

^a Blending was carried out at 70°C for 30 min.

^b Weight of Starch-Cl/PCL blend/(weight of starch-Cl + weight of PCL).

^c Light brown.

To check the chemical reaction between chloride group in starch-Cl and hydroxyl group in PCL, the FTIR spectra of the starch-Cl/PCL blend was measured. The results are shown in Figure 2. In FTIR results, unblended PCL showed a sharp peak around 1710 cm^{-1} for the internal ester group and a weak peak around 3400 cm^{-1} for the hydroxyl group, re-

spectively. By blending starch-Cl and PCL, the FTIR spectrum (sample No. II-11) showed three distinct new peaks (marked by arrows in Fig. 2) at around 3400, 1650, and 1050 cm^{-1} relative to that of PCL. The peaks at 3400 and 1650 cm^{-1} represent the hydroxyl and internal —C—O—C— ascribed in starch. Also, the peak at 1050 cm^{-1} represents the ether linkage as

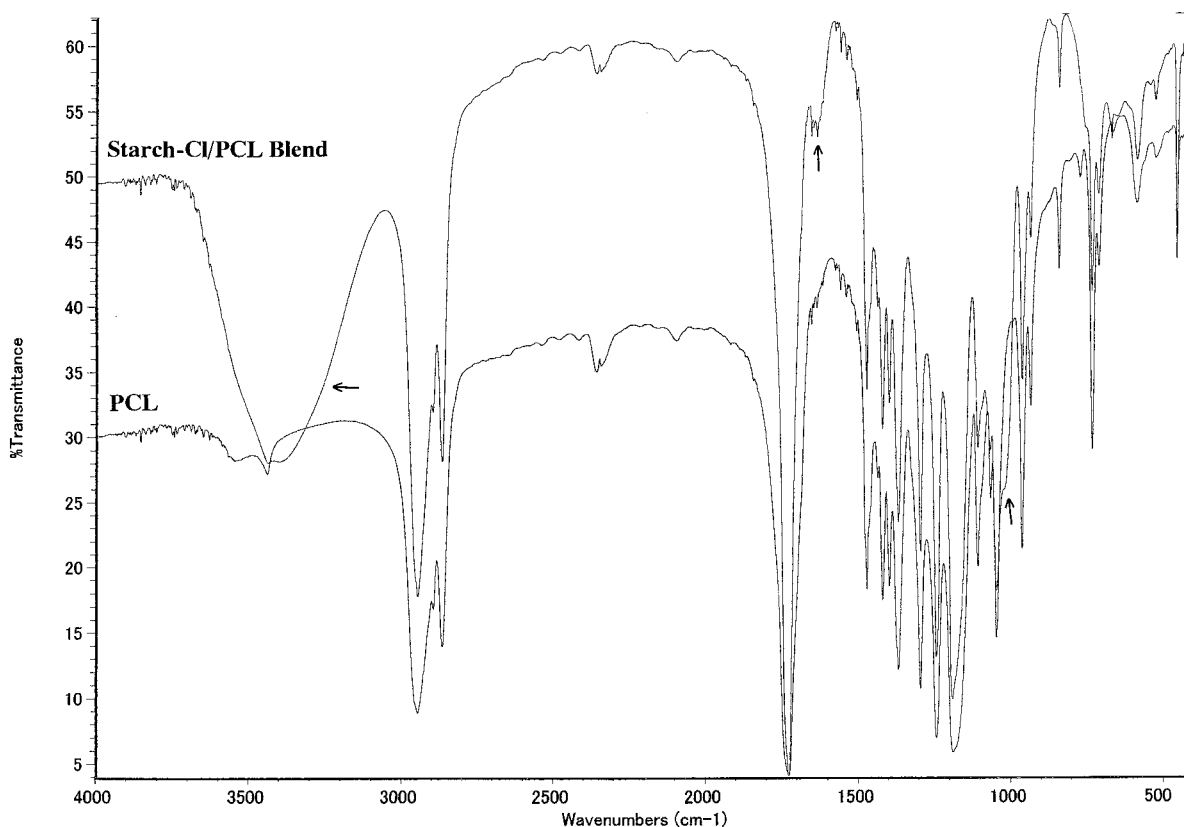


Figure 2 FTIR spectra of PCL and starch-Cl/PCL blend.

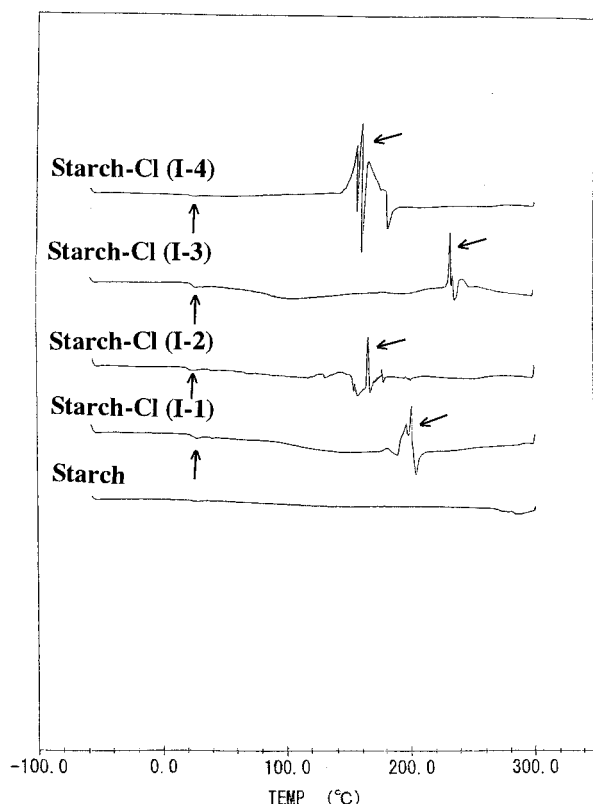


Figure 3 DSC thermograms of starch and starch-Cl's.

indicated in the chemical reaction between starch-Cl and PCL. The FTIR spectra of other blend samples (sample Nos. II-4~10) were similar to that of previous results (data not shown).

Thermal characteristics

Thermal properties of starch-Cl

The thermal characteristics for starch and starch-Cl prepared with different reaction temperatures and times were given in Figure 3. As shown in Figure 3, the DSC curve of starch did not show any characteristic peak ascribed in first-order transition (melting transition) and second-order transition (glass transition). Generally, in the case of polysaccharides, to show the first-order transition (melting transition) in DSC curve, sufficient water content was needed. However, water content of starch used in our study was very low, about 11%. So, any characteristic peak was not detected in DSC results. By chlorination of starch, however, the thermal characteristic peak could be clearly shown on the DSC thermograms. The characteristic peaks ascribed in glass transition for all starch-Cl's appeared commonly around 30°C regardless of degree of chlorination (marked by an arrow in Fig. 3). Also, sharp exothermic peaks ascribed in degradation of chloride group attached in starch molecule were

shown in the DSC curve (marked by an arrow in Fig. 3). According to increasing the chloride content in the starch molecule, the sharp exothermic peaks were shifted to a lower temperature (230~170°C). These results supported the finding that, by introducing chloride group in starch, starch became less stable; thereby, thermal stability was decreased. The DSC curve of starch-Cl (sample No. I-5) was similar to that of starch-Cl (sample No. I-4) (data not shown).

Thermal properties of starch-Cl/PCL blend

The thermal characteristics for the PCL, starch/PCL mixture, and starch-Cl/PCL blends were measured by DSC; the results are given in Figure 4. Also, major characteristic peak temperatures and enthalpy value of based PCL part during melting obtained in DSC results are shown in detail in Table III.

Here, the mixture was prepared by merely mixing starch and PCL with a weight ratio of starch/PCL of 1/2. As shown in Figure 4, the DSC curve of PCL shows a sharp endothermic peak at 66°C ascribed in melting transition; the mixture having a weight ratio of starch/PCL 1/2 shows only a sharp endothermic peak at 65°C but showed very few characteristic peaks as similar to PCL. However, by blending PCL with starch-Cl (sample No. II-11), the sharp endothermic peak representing the melting of PCL shifted to a lower temperature as well as the newly weak glass

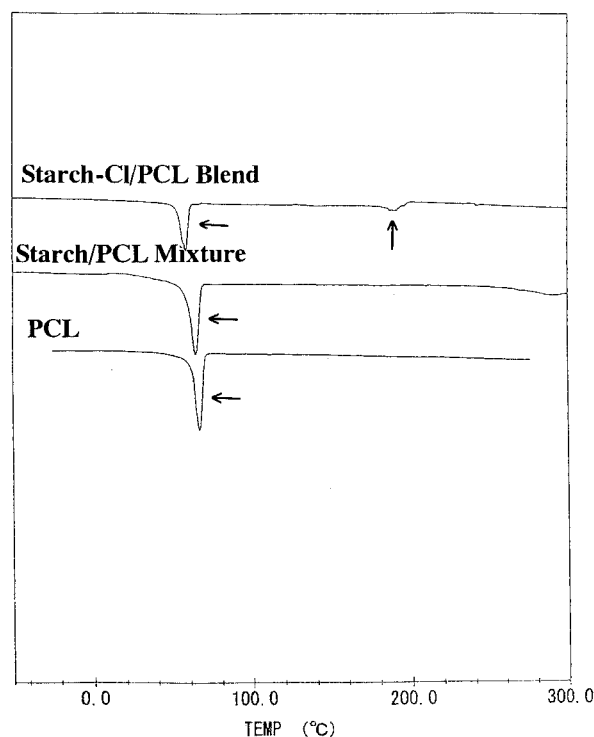


Figure 4 DSC thermograms of PCL, starch/PCL mixture, and starch-Cl/PCL blend.

TABLE III
Melting Point (T_m) and Enthalpy Value (ΔH_m) of Starch/PCL Mixture and Starch-Cl/PCL Blends Originated in PCL Component

Sample	PCL	Mix ^a	Starch-Cl/PCL blend							
			II-4	II-5	II-6	II-7	II-8	II-9	II-10	II-11
T_m (°C)	66.61	65.12	61.20	58.96	61.90	59.95	60.05	57.90	61.24	58.91
ΔH_m (J/g)	72.39	70.51	50.45	49.12	50.99	50.12	50.01	47.54	50.05	48.05

^a Mixture was prepared by merely mixing starch and PCL with wt ratio of starch/PCL, 1/2.

transition peak appeared around 200°C in the DSC curve. This glass transition peak was ascribed in starch attached in PCL; it was introduced by a chemical reaction between Cl in starch-Cl and hydroxyl group in PCL. The other starch-Cl/PCL blend samples (sample No. II-4–10) showed similar DSC results to that of the starch-Cl/PCL blend (sample No. II-11) (data not shown).

As shown in Table III representing the enthalpy value on melting of pure PCL, starch/PCL mixture, and starch-Cl/PCL blend, the enthalpy values for pure PCL and the starch/PCL mixture were 72.39 and 70.51 J/g, respectively, shown as a similar value to each other. However, enthalpy values of starch-Cl/PCL blends were about 47.54–50.99 J/g, shown as much smaller values rather than those of pure PCL and starch/PCL mixture. This value was supposed to be the result of the chemical reaction between chloride group in starch-Cl and hydroxyl group in PCL, the reciprocal action between crystalline region of PCL, and the amorphous region of starch occurring in the starch-Cl/PCL blend. From this result, it was confirmed that the starch-Cl/PCL blend had high miscibility between starch and PCL.

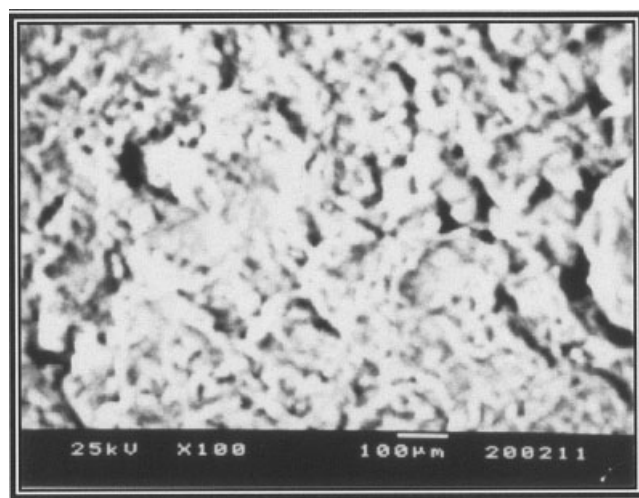
Morphologic characterization

To check the morphology of the starch-Cl/PCL blend, SEM was measured; the results are given Figure 5. Starch-Cl/PCL blends (sample No. II-11) did not show any aggregated particle and it can be observed that the starch granule was holding a small size and was well distributed in the PCL matrix, confirming a good interconnection between starch and PCL phases [Fig. 5(A)]. As shown in Figure 5(B) especially, measured by high magnification ($\times 1000$), it was observed distinctly that the starch granule was embedded well in PCL matrix because the starch granule did attach by chemical reaction.

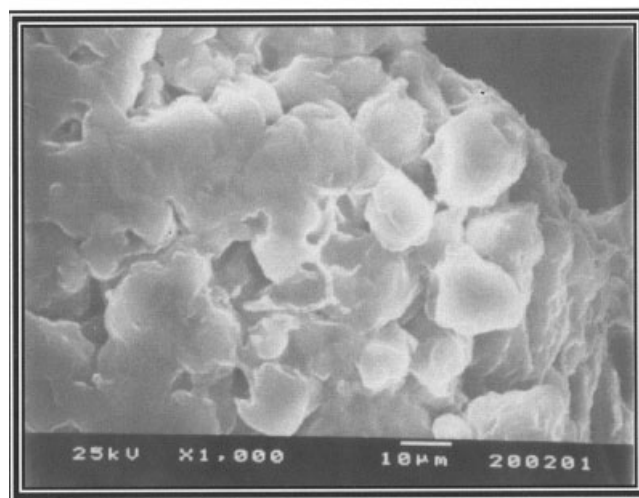
Solvent resistance

The solvent resistance of native cornstarch and starch-Cl/PCL blend in DMSO, distilled water, alkaline, and acidic solution is shown in Table IV. It was impossible to measure the solvent resistance of starch to DMSO

because of its high solubility. While the solvent resistance of starch showed 0.67 in water, 0.40 in NaOH, and 0.61 in HCl, respectively, that of starch-Cl/PCL blend (sample No. II-11) showed higher values (0.50 in



(A)



(B)

Figure 5 SEM of starch-Cl/PCL blend.

TABLE IV
Solvent Resistance of Native Corn Starch, PCL, and Starch-Cl/PCL Blend in Various Solvents^a

Solvent	Sample		
	Starch	PCL	Starch-Cl/PCL blend (sample No. II-11)
DMSO	— ^b	0.60	0.50
Water	0.67	0.95	0.92
0.5N NaOH	0.40	0.96	0.61
0.5N HCl	0.60	0.95	0.77

^a Measured as weight ratio of insoluble residue before and after dispersing the sample in solvent (0.1 g/25 mL) at 30°C for 24 h.

^b Not able to measure due to high solubility.

DMSO, 0.92 in water, 0.61 in NaOH, and 0.77 in HCl) than that of starch, showing a similar value of PCL.

CONCLUSION

In this study, starch-Cl/PCL blend with high miscibility could be prepared easily by mixing starch-Cl and PCL in a homogeneous state. By using higher DS of starch-Cl or strong alkaline media, the yield of starch-Cl/PCL blend increased because of the high chemical reaction between starch-Cl and PCL. By this chemical reaction, the miscibility between starch and PCL was increased. From these results, we found that this starch-Cl/PCL blend was supposed to be useful as biodegradable plastic material in various industrial fields. We will report the results of the mechanical strength of this blend sample obtained through compress mold or extruder soon.

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