Substitution of Corn Starch With Polycaprolactone via Chlorination and Water Resistance of the Substituted Starch

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ABSTRACT: Corn starch was chlorinated using methanesulfonyl chloride in dimethylformamide (DMF) and then substituted with polycaprolactone (PCL) in various solvents [dimethylsulfoxide (DMSO), water and dimethylacetamide (DMAc)] containing a catalyst [sodium hydroxide (NaOH) or lithium chloride (LiCl)] to improve water resistance. The reaction yield based on the product weight was highest (85%) when DMAc and LiCl were used. Fourier transform infrared (FTIR) spectra showed that starch was monosubstituted with PCL in the aqueous NaOH solution, whereas it was to crosslink by PCL in the case using DMAc and LlCl. The intrinsic viscosity of the products in DMSO supports these trends. By introducing the hydrophobic PCL onto starch, solvent resistance of the substituted starches to water and other aqueous media increased. The crosslinked starch displayed higher water resistance than the monosubstituted starch. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2197–2202, 2001

Key words: monosubstituted starch with PCL; crosslinked starch with PCL; chlorinated starch

INTRODUCTION

Disposable commodity plastics used in various purposes such as fast-food packaging and agricultural film draw public attention because of their environmental accumulation without degradation. Their lack of degradability impacts on the depletion of landfills, as well as the water and soil litter problem. There has been intense research activity either to modify current plastic products to enhance degradability or to develop new, suitable, alternative materials that are degradable.[1–4] In this respect, biodegradable polyesters produced by bacteria or organic synthesis, such as

polycaprolactone (PCL), aliphatic polyesters, polyhydroxybutyrate (PHB), and polyhydroxyvalerate (PHV), are of considerable technological importance for the use as commodity plastics as well as special polymers in medical applications.[5] But these degradable polyesters are very expensive to produce; thus, it is unlikely that they will replace conventional thermoplastics in applications in which large quantities of material are deployed.[6]

By contrast, starch, one of the natural biodegradable polymers obtained from agricultural crops, is produced at a relatively low price.[7] This natural polymer is currently used as a raw material or an ingredient in degradable or decomposable plastic products.[8,9] In addition to the degradability, incineration of the starch-based products may not cause global warming.

However, starch by itself exhibits poor mechanical properties although plastic processing may be possible solely with starch using high

technique. It is sensitive to moisture, poor in storage stability, and difficult to process in common process.[10,11] In order to overcome these drawbacks, blending or grafting with synthetic and hydrophobic polymers, such as polyethylene, poly(vinylalcohol), poly(vinylchloride), and poly-(ethylene-co-acrylic acid) copolymer, has been recommended.[12–18]

Despite a variety of approaches, the improvements in physical performance were not significantly accomplished in starch/polymer blend systems. In these blended systems, two major common drawbacks have been pointed out: the incompatibility between starch and synthetic polymers, and the reduction of biodegradability of the systems by the incorporated synthetic polymer. Therefore, grafting or compatible blending with a degradable polymer could be more effective and practical approach. Among degradable polyesters, polycaprolactone (PCL) is of interest for use in modifying material in blend because of its high compatible, hydrophobic, and mechanical properties. As an example, corn starch has been grafted with polycaprolactone (PCL), using a urethane reaction to improve the hydrophobic, mechanical properties but not to decrease the biodegradability.[19,20]

In this study, corn starch was chemically substituted with PCL via chlorination under several reaction conditions. The changes in structural and physical properties such as intrinsic viscosity and solvent resistance of the products were investigated.

EXPERIMENTAL

Materials and Reagents

Corn starch and PCL terminated with hydroxyl groups (number-average molecular weight: 1250) were purchased from Aldrich Chemical Company (Milwaukee, WI). Sodium hydroxide (NaOH) and lithium chloride (LiCl) were purchased from Tokyo Kasei Co. (Tokyo, Japan). Methanesulfonyl chloride (CH_3SO_2Cl), dimethylsulfoxide (DMSO), and dimethylacetamide (DMAc) were purchased from Junsei Chem. Co. Ltd. (Tokyo, Japan). All other chemicals were reagent grade and used without further purification.

Preparation of Chlorinated Starch (Starch–Cl)

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. Methanesulfonyl chloride (CH_3SO_2Cl, 50~100 mL) was slowly added for 1 h into the reaction mixture while stirring at a temperature of 40, 50, or 60°C, and the reaction mixture was continuously stirred for 10–20 h at the controlled temperature. The reacted starch was precipitated by adding excess acetone (500–1000 mL) and then collected by a vacuum filtration (Whatman No. 1003). The residue was washed several times with acetone, and then dried in a vacuum oven (40°C) overnight.

Preparation of PCL-Substituted Starch (PS)

The starch–Cl (chlorine content: 16.5%) was reacted with PCL according to three different procedures (PS-1, 2, and 3).

PS-1 Using DMSO and NaOH

PCL (2 g) was dissolved in DMSO (95 mL) by stirring over 30 min at 60°C. Freshly powdered NaOH (4 g) was added, and then the mixture was strongly stirred over 30 min under N_2. Starch–Cl/DMSO solution (1 g/5 mL), which had been prepared separately, was slowly added to the PCL solution for 30 min while maintaining the temperature at 60°C. Stirring was continued for 1 h after the addition. Excess water (1 L) was added into the mixture, and then the reacted starch (PS-1) was recovered by filtration (Whatman No. 1003). The residue was washed with water (300 mL) and chloroform (300 mL) to remove the unreacted starch–Cl and PCL, respectively. Finally, the PCL-substituted starch was dried in a vacuum oven (40°C) overnight.

PS-2 Using Water and NaOH

For preparation of PS-2, distilled water was used instead of DMSO; other conditions were the same as used for the preparation of PS-1. Unlike the procedure for PS-1, however, the substituted starch product gradually precipitated in the reaction solution. The precipitate (PS-2) was recovered by vacuum filtration (Whatman No. 1003), and the residue was washed and dried as described in PS-1 preparation.

PS-3 Using DMAc and LiCl

LiCl (4.2 g) was added to DMAc (95 mL); the mixture was then stirred for 1 h at room temperature. PCL (2 g) was added to the solution, and
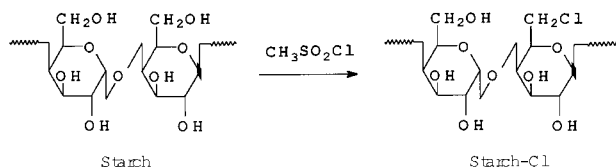
Scheme I   Preparation of starch–Cl.

the mixture was vigorously stirred for 30 min at 60°C under N_2. Starch–Cl/DMAc (1 g/5 mL) solution, which had been prepared separately, was slowly added to the PCL solution for 30 min while maintaining the temperature at 60°C. The stirring was continued for 1 h after the addition. As the reaction progressed, the product was gradually precipitated in reaction solution. The precipitate (PS-3) was recovered by a vacuum-filtration (Whatman No. 1003), and the residue was washed and dried as described in the PS-1 preparation.

Structure Characterization

FTIR spectra were obtained with KBr pellets of the native and substituted starches using an FTIR spectrometer (Perkin–Elmer Spectrum GX, Beaconsfield, UK). Chlorine content in starch–Cl was measured with an elemental analyzer (Carlo Erba, Milan, Italy).

Intrinsic Viscosity (η)

Intrinsic viscosity (η) of the PCL-substituted starches was measured in DMSO at 30°C using an Ubbelohde viscometer.[21] Sample concentration in DMSO was within the range of 0.0035–0.0414 (g/dL).

Solvent Resistance

Native starch, starch–Cl, or PCL-substituted starch was dispersed in various solvents (25 mL); the dispersion was then vigorously stirred at 30°C for 48 h. The solvents tested included DMSO, pure water, and 0.5N NaOH or HCl solution. The undissolved residue was filtered (Whatman No. 1003), and then dried in a vacuum oven for weight measurement. The solvent resistance was calculated by the following equation:

Solvent resistance (%) =

$$\frac{\text{Dry weight of residue after filtration}}{\text{Dry weight of initial sample}} \times 100$$

$$(1)$$

RESULTS AND DISCUSSION

Chlorination of Starch

The chlorination reaction of starch is briefly shown in Scheme I, and the chlorine contents in the chlorinated starches (starch–Cl) under various reaction conditions are shown in Table I. When the cornstarch was chlorinated using methylsulfonyl chloride (CH_3SO_2Cl) at 40°C or 50°C, the chlorine content was relatively small, but at 60°C, it increased more than 3 times. When the reaction was carried out at 60°C with 100 mL of the chlorination agent and 15 g of starch, the chlorine content after 10 h of reaction increased only by 4% in comparison with that after 5 h. But a reduced content of the agent (50 mL) and increased reaction hour (15 vs 10 h) did not show a significant change in the chlorine content. The starch–Cl prepared at 60°C was colored in dark brown, whereas it was much less colored at lower reaction temperatures. The chlorination agent (50 mL CH_3SO_2Cl) used contained 23.3 g chloride. This amount was much higher than that of the starch (15 g) used for the reaction. Therefore, the chlorination efficiency based on the reaction yield was significantly low under the experimental conditions.

An FTIR spectrum of a chlorinated starch (starch–Cl) prepared at 60°C by 5 h reaction is shown in Figure 1. The native starch showed a typical broad peak for the hydroxyl groups in starch at approximately 3400 cm^{-1} (marked by an arrow in Fig. 1). By chlorination, the FTIR spectrum of the starch became changed displaying a new broad peak at ~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. (marked by an

Table I   Chlorine Content (*CC*) in Starch-Cl Prepared Under Various Reaction Conditions[a]

MeSO$_2$Cl (mL)	Time (h)	Temp (°C)	*CC*[b] (%)
100	20	40	5.3
100	15	50	5.5
100	5	60	16.5
100	10	60	20.5
50	15	60	19.3

[a] Starch and DMF contents were 15 g and 150 mL, respectively.
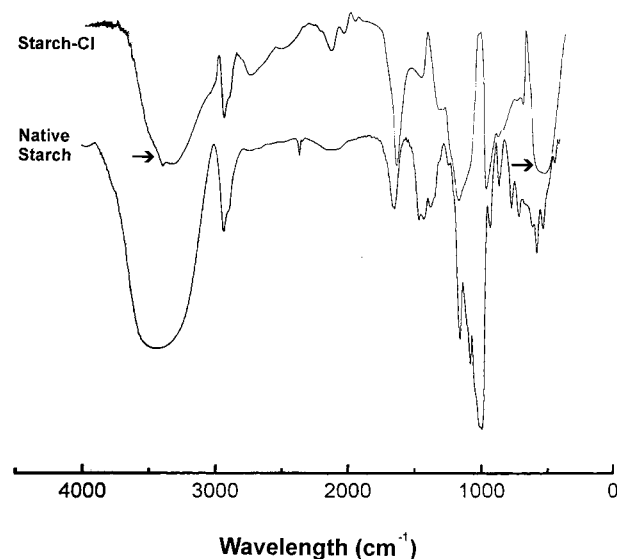[b] Calculated by elementary analysis.

Figure 1 FTIR spectra of native and chlorinated (starch–Cl) starches.

arrow in Fig. 1). At the same time, the hydroxyl peak at ~ 3400 cm^{-1} was substantially decreased by the chlorination, indicating the presence of the substitution on the hydroxyl groups.

PCL Substitution of Starch

The substitution of starch with PCL is briefly shown in Scheme II. A is prepared using DMSO and NaOH as the reaction solvent and catalyst, respectively. B is prepared using water, NaOH and DMAc, LiCl, respectively. The approximate production yield, calculated from the weight ratio between the product and the reactants, was sig-
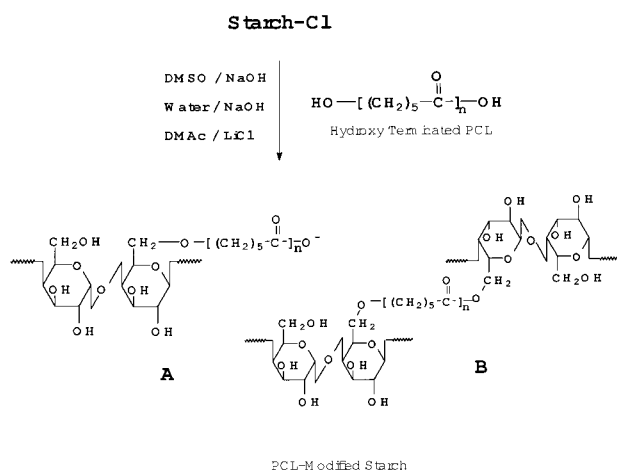

Scheme II Preparation of polycaprolactone (PCL)-substituted starches

Table II   Yield of the PCL-Substituted Starches (PS) Under Various Reaction Conditions*

PS	Solvents (mL)	Catalysts (g)	Yield[a] (%)
PS-1	DMSO (100)	NaOH (4.0)	5
PS-2	Water (100)	NaOH (4.0)	58
PS-3	DMAc (100)	LiCl (4.2)	85

* Reaction was carried out at 60°C for 1 h with 1 g of starch–Cl and 2 g of PCL.
[a] Weight of PS/(weight of starch–Cl + weight of PCL).

nificantly changed according to the reaction conditions (Table II). When DMSO and NaOH were used as the reaction solvent and catalyst, respectively, the reaction yield was only about 5%. However, when distilled water was used instead of DMSO, the reaction yield substantially increased up to about 58%. This was because NaOH was almost insoluble in DMSO but was fully soluble in water. A strong alkaline condition was required for the catalytic action on the hydroxyl substitution. When DMAc and LiCl were used for the reaction, the reaction yield (85%) was higher than that obtained in water and NaOH.
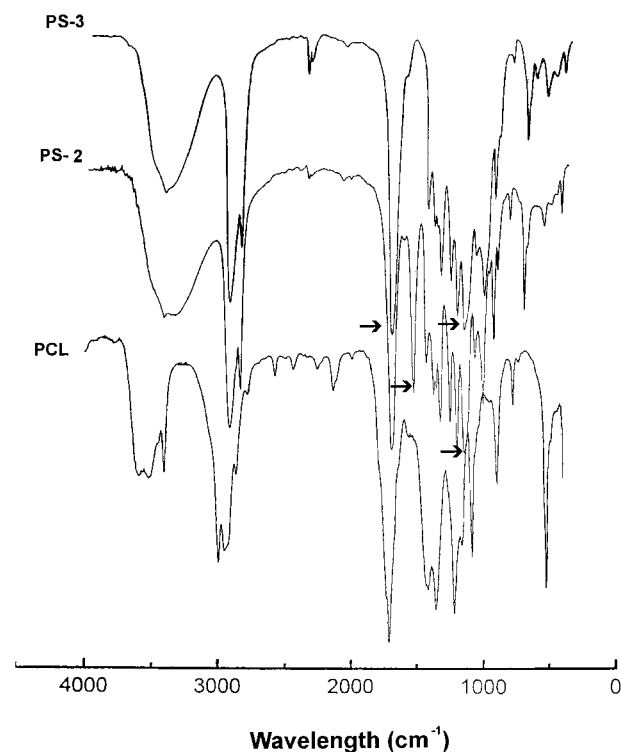

Figure 2 FTIR spectra of polycaprolactone (PCL) and PCL-substituted starches (PS-2 and 3).

Table III Intrinsic Viscosity (η)[a] of Native Corn Starch, Starch–Cl, and PCL-Substituted Starches (PS)

	Starch	Starch-Cl	PS-1	PS-2	PS-3
η (dL/g)	7.55	7.57	8.56	8.58	9.61

[a] Measured using an Ubbelohde viscometer in DMSO at 30°C.

FTIR spectra of the PCL-substituted starches are shown in Figure 2. By the reaction with PCL in water and NaOH medium (PS-2), the FT-IR spectrum of the modified starch showed three distinct new peaks (marked by arrows in Figure 2) at around 1200, 1600, and 1730 cm^{-1}. The peaks at 1200 and 1600 cm^{-1} represent ether linkages between starch and PCL and the carboxyl groups at the terminal of the substituted PCL chains, respectively. The peak at 1730 cm^{-1} represents the ester linkages inside the PCL chains. Like chlorination, substitution with PCL on starch, the peak intensity of the hydroxyl groups in starch (3400 cm^{-1}) was reduced. The FTIR spectrum of PS-1 was similar to that of PS-2.

By substitution of starch with PCL using DMAc and LiCl (PS-3), spectrum showed the peaks at around 1730 cm^{-1} and 1200 cm^{-1}, representing the ester and the ether linkages, respectively. However, the peak at ~1600 cm^{-1} that had been shown in PS-1 or PS-2 was not displayed. From this difference, it was supposed that the PCL-substituted starch prepared in DMSO or distilled water in the presence of NaOH formed mainly monosubstituted starch–PCL copolymers (Scheme IIA). The absence of a 1600-cm^{-1} peak representing the carboxyl terminal of PCL indicates that both terminals of a PCL chain were linked to starch. Therefore, the PCL chain crosslinked the starch molecules (Scheme IIB).

Intrinsic Viscosity (η)

As shown in Table III, η of the starch–Cl was 7.57 dL/g. This value was almost the same as that of the native starch (7.55 dL/g). This result might indicate that there were not any significant degradations of starch during the chlorination.

By PCL substitution, η of PS-1 and PS-2 was slightly increased from 7.55 to 8.56 and 8.58 dL/g, respectively. But η of PS-3 was significantly higher (9.61 dL/g) than that of PS-1 or PS-2. The viscosity data agreed with the suggestion based on the FTIR spectra, in which PS-1 and PS-2 were monosubstituted whereas PS-3 was crosslinked with PCL.

Solvent Resistance

The solvent resistance of native starch and PCL-substituted starches in DMSO, water, and alkaline or acidic solution is shown in Table IV. It was impossible to measure the solvent resistance of starch–Cl because of its high solubility in all the solvents used. Native starch and all the PCL-substituted starches were soluble in DMSO. In aqueous solutions or pure water, the PCL substitution exhibited increased solvent resistances: from 0.40 to 0.56–0.61 in 0.5 N NaOH, 0.61 to 0.72–0.75 in 0.5 N HCl, and 0.67 to 0.80–0.90 in water. Among the tested solvents, resistance of the PCL-substituted starch was highest in pure water. Crosslinked product (PS-3) displayed slightly higher resistances than the monosubstituted products (PS-1 and 2). However, the difference was relatively small. The raised solvent resistance by the PCL-substitution was caused by the inherent hydrophobicity of the substituted

Table IV Solvent Resistance[a] of Native Corn Starch, Starch–Cl, PCL, and PCL-Substituted Starches (PS) in Various Solvents

	Starch	Starch-Cl	PCL	PS-1	PS-2	PS-3
DMSO	—[b]	—	0.23	—	—	—
Water	0.67	—	0.90	0.80	0.82	0.90
0.5N NaOH	0.40	—	0.91	0.56	0.59	0.61
0.5N HCl	0.61	—	0.90	0.75	0.72	0.75

[a] Measured as weight ratio of insoluble residue before and after dispersing the starch in solvent (0.1 g/25 mL) for 24 h at 30°C.
[b] Not able to measure due to the high solubility.

PCL chains. The resistance to water and aqueous solutions is beneficial in a variety of applications of the polymer as a degradable plastic material.

CONCLUSIONS

PCL substitution of corn starch could be carried out effectively by using chlorinated starch, and in an aqueous alkaline solution or DMAc containing LiCl. Starch was monosubstituted when aqueous NaOH solution was used, whereas it was crosslinked when DMAc and LiCl were used. In both cases, the PCL substituents increased solvent resistances of starch, especially to water and aqueous acidic or alkaline solutions.

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