

Syntheses of Chemical-Modified Cellulose Obtained from Waste Pulp

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ABSTRACT: Chemical-modified pulps were synthesized from four types of waste pulps (Pulp1–4) and succinic anhydride (SAn) or maleic anhydride (MAn). The solubility of the modified pulps was evaluated in common organic solvents, and their thermal properties were investigated by DSC measurement. The solubility of the modified pulps increased with an increasing degree of substitution (DS). However, no T_g or T_m of these modified pulps was confirmed. Pulps and modified pulps were graft-polymerized with ϵ -caprolactone (CL) in bulk and in DMAc/LiCl. Although the solubility of the graft copolymers was similar to

modified pulps, some graft copolymers showed a T_g by the introduction of CL units. In the bulk, graft copolymers obtained from modified pulps and nonmodified pulps showed a T_g of about 75°C and no T_g , respectively. In DMAc/LiCl, the obtained graft copolymers from both modified and nonmodified pulps exhibited a T_g of 95–110°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2059–2065, 2003

Key words: polysaccharides; waste; modification; glass transition; graft copolymers

INTRODUCTION

Waste pulp is short fibril cellulose produced from the manufacture of paper. Waste pulp has been generally disposed of by burning or burying. If biodegradable materials are prepared from waste pulp, the production cost can be lowered and the amount of CO₂ will be reduced. However, it is difficult to prepare biodegradable plastics from cellulose because cellulose strongly combines neighboring cellulose molecules by strong hydrogen bonds between hydroxyl groups due to three hydroxyl groups per glucose unit. Because of the strong hydrogen bonds, cellulose has no glass transition points (T_g) or melting points (T_m) and is hardly soluble in common solvents, although cellulose is a linear polymer.

Chemical modification of cellulose is one of the methods to give thermoplasticity and solubility. Intermolecular hydrogen bonds of cellulose become weak by steric hindrance of the substituents. Also, the cellulose chain is disorganized by the introduction of substituents. Thus, modified celluloses are improved to show good solubility and reactivity as well as certain T_g and T_m . Nitrocellulose and cellulose acetate are typical thermoplastic cellulose derivatives bearing low

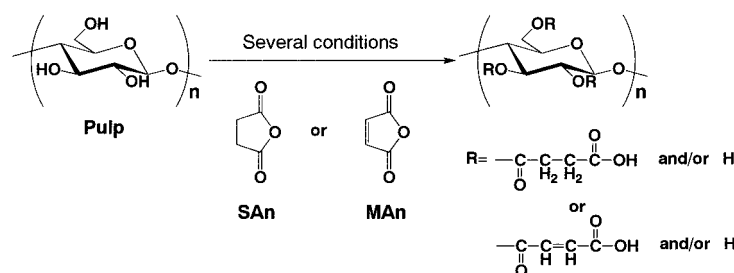
molecular weight substituents on the site of hydroxyl groups in the glucose unit.^{1,2} They were developed more than one century ago and had been widely used until synthetic plastics were advanced in the first half of the 20th century. In addition to them, methyl-, ethyl-, carboxymethyl-, and hydroxyethyl celluloses have also been well known.^{3–8}

On the other hand, many articles on thermoplastic cellulose derivatives bearing high molecular weight substituents have also been published. For example, Wang and Tao synthesized cellulose–fatty acid esters using some long-chain fatty acid chloride and reported their thermal properties, solubilities, and biodegradabilities.⁹ Stannett et al. synthesized block copolymers by the reaction of cellulose acetate with diisocyanate such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) and reported that these products have a softening point and biodegradability.¹⁰

To give thermoplasticity to waste pulp, we focused on succinic anhydride (SAn), maleic anhydride (MAn), and ϵ -caprolactone (CL) as chemically modifying reagents. SAn is used to prepare biodegradable copolymers.¹¹ We expected that succinyl groups or maleyl groups were easily introduced onto glucose units by use of SAn or MAn due to the high reactivity of acid anhydride. Thermoplasticity may be given by a decrease of the crystallinity of waste pulp due to the steric effect of substituents. Moreover, the carboxylic acid derivatives may give an increase of the waste

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Scheme 1

pulp. CL is a cyclic monomer that forms one of the typical biodegradable plastics called poly(CL) (PCL). Because of the low T_m of the PCL homopolymer, PCL is usually blended with other biodegradable polymers having a high T_m or copolymerized with other monomers.^{12,13} Therefore, graft copolymerizations of cellulose with PCL can be expected to overcome both the weak points of cellulose and PCL. In this article, we used four types of waste pulp as cellulosic materials and synthesized chemically modified celluloses from SAn or MAN and/or CL and discuss their reactivities, solubilities, and thermal properties.

EXPERIMENTAL

Purification of waste pulp

Purified pulps (Pulp2–4) were obtained as follows: Pulp2 was obtained by refluxing original waste pulp (Pulp1) in a 3N HCl aqueous solution for 3 h, Pulp3 was obtained by refluxing Pulp1 in water for 3 h, and Pulp4 was obtained by refluxing Pulp3 in a 2N HCl aqueous solution for 3 h.

Syntheses of cellulose succinate (PSA) and cellulose maleate (PMA) (Scheme 1)

The typical synthetic procedure was as follows: Pulp4, 0.5 g (3.1 mmol), and pyridine, 15 mL, were placed in a four-neck flask and stirred at 100°C for 3 h under a nitrogen atmosphere. Then, SAn, 0.93 g (9.3 mmol), was added and stirred at 100°C for 24 h under a nitrogen atmosphere. After the reaction, the product was poured into excess ethyl acetate to remove the unreacted SAn and filtered *in vacuo*. Then, the product

was fully washed with ethyl acetate, filtered, and dried *in vacuo*.

Syntheses of cellulose–poly(ϵ -caprolactone) graft copolymer (Pulp-g-PCL) (Scheme 2)

In bulk

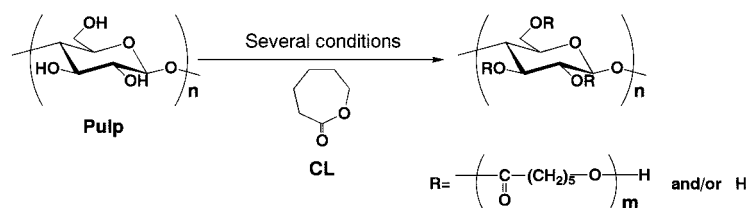
The typical synthetic procedure was as follows: Pulp4, 2.0 g, CL, 20 mL, and tin(II) 2-ethylhexanoate (Sn-oct), 0.3 g, were placed in a pear-shaped flask and stirred at 110°C for 24 h under a nitrogen atmosphere. After the reaction, chloroform was added to the flask and stirred, then filtered. The product was thoroughly washed with chloroform, filtered, and dried *in vacuo*.

In solution

The typical synthetic procedure was as follows: Pulp4, 1.0 g, *N,N*-dimethylacetamide (DMAc), 10 mL, and lithium chloride (LiCl), 0.08 g, were placed in a pear-shaped flask and stirred at 80°C for 24 h under a nitrogen atmosphere. After cooling at room temperature, 6 mL of CL was added and stirred at 100°C for 24 h under a nitrogen atmosphere. After the reaction, chloroform was added to the flask and stirred, then filtered. The product was thoroughly washed with chloroform and dried *in vacuo*.

Measurements

An IR spectrum was taken on an FTIR-8100A (Shimadzu) spectrometer by a KBr disk. X-ray diffraction was measured with an X-ray diffractometer XR-D1 (Shimadzu). DSC measurement was accomplished on



Scheme 2

a DSC 3100 equipped with MTC 1000S (MAC Science). The melting point was measured with a Mettler FP82HT hot stage equipped with a Mettler FP80 HT central processor (Mettler) and an Olympus Model PM-10-M (Olympus) apparatus. Press molding of the graft copolymers was performed using a Yuatu Power P-1-B (Riken Seiki) and Tablet Molder (Jasco) apparatus.

Materials

Solvents for all the reactions were purified by general procedures. Microcrystalline cellulose (Avicel #2331, Merck) was used as received. Waste pulp was supplied by the Murakami Shoji Co. Ltd.

RESULTS AND DISCUSSION

Purification of waste pulp

Pulp1 was the original waste, Pulp3 was fibril, and Pulp2 and Pulp4 were powders because of acid hydrolysis of the amorphous parts in the cellulose molecules. XRD diagrams of commercial microcrystalline cellulose (Avicel, MC) and Pulp4 are shown in Figure 1. In Figure 1, peaks of Pulp4 (B) were similar to those of MC (A) as a whole, but rougher than those of MC. This suggests that Pulp4 had similar crystal structures to those of MC, but a particle size for Pulp4 was more dispersed than for MC. Moreover, MC was soluble in DMAc/LiCl; on the contrary, Pulp4 was only partially soluble in it. This also may be supported by the XRD result.

Syntheses and properties of PSA and PMA

Reaction conditions, yields, and degrees of substitution (DS, max = 3.0) are shown in Table I. All the reactions proceeded heterogeneously through the reaction. IR spectra of Pulp4 and succinated-Pulp4 (P4SA) are shown in Figure 2. The progress of the reaction was confirmed by the appearance of the peak around 1750 cm^{-1} due to the carbonyl groups of succinate.

To study the difference of reactivity, the DS values of the chemical-modified cellulose under several conditions are discussed. Figure 3 shows DS data based on Table I. From Figure 3, the reaction using SAN proceeded easier than when using MAN, and the DS values of PSA became higher than those of PMA. Because of the double bond of MAN, MAN is more stable than is SAN. Thus, it may be expected that Pulp reacted more easily to SAN than to MAN.

The order of the reactivity of cellulosic materials was Pulp3 > Pulp1 > Pulp4 > Pulp2. The reactivity on the amorphous part of cellulose is higher than on the crystalline part because hydrogen bonds are dis-

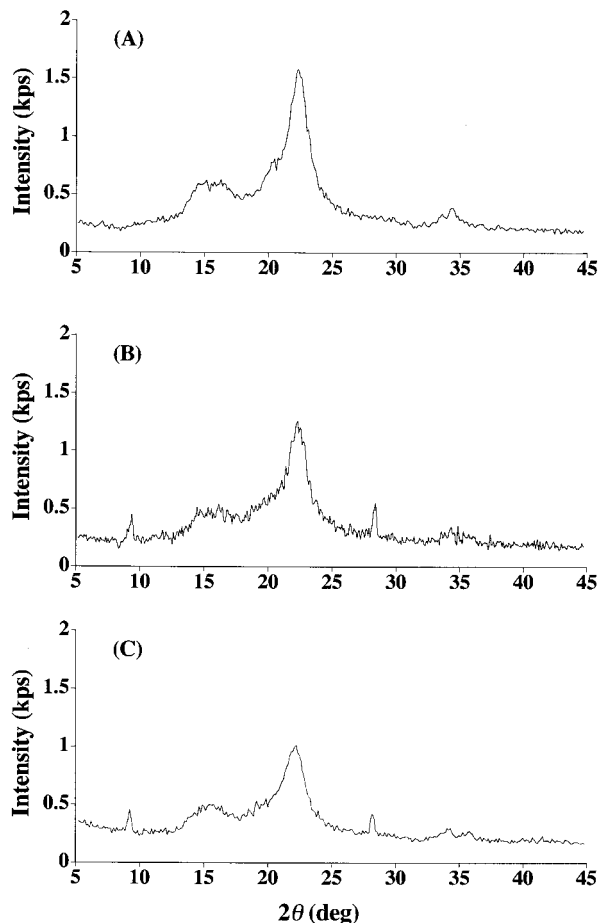


Figure 1 X-ray diffraction diagrams for (A) microcrystalline cellulose, (B) Pulp4, and (C) P4SA (DS = 1.29).

ordered on the amorphous part. Therefore, Pulp1 and Pulp3 exhibited higher reactivity than that of Pulp2 and Pulp4. The difference of reactivity between Pulp1 and Pulp3 was due to their forms: block or fibril. The difference of reactivity between Pulp2 and Pulp4 was due to the concentration of HCl aqueous on the purification of waste pulp.

Considering the effect of the reaction medium on the DS values, the order of the DS values was pyridine > DMAc/LiCl > toluene. This result may be due to the difference in the solubility of cellulose in the medium and the catalysis of pyridine. The peak intensity of P4SA shown in Figure 1 was slightly weaker than that of Pulp4, suggesting that the crystallinity decreased by the introduction of succinyl groups on the cellulose.

Solubility of Pulp4 and P4SA (DS = 0.37 and 1.29) in several solvents is shown in Table II. P4SA (DS = 0.37) was partially soluble or swelled in chloroform, toluene, and THF. Moreover, P4SA (DS = 1.29) was soluble in DMAc/LiCl and partially soluble or swelled in methanol and acetone as well as in chloroform, toluene, and THF. This suggests that the introduction of

TABLE I
Syntheses of Pulp Derivatives

Run	Pulp ^a (g, mmonomol)	Reagent (g, × 10 ⁻² mol)	Medium ^b (mL)	Temperature (°C)	Time (h)	Yield (g)	DS ^d
1	1 (0.5, 3.1)	SAn(0.93, 0.93)	Py. (10)	100	24	0.74	1.41
2	2 (0.5, 3.1)	SAn(0.93, 0.93)	Py. (10)	100	24	0.50	1.02
3	2 (0.5, 3.1)	SAn(4.7, 4.7)	Tol. (20)	100	40	0.47	0.40
4	2 (0.5, 3.1)	SAn(4.7, 4.7)	DMAc (25) ^e	100	24	0.32	1.37
5	3 (0.5, 3.1)	SAn(0.93, 0.93)	Py. (10)	100	24	0.71	1.35
6	3 (0.5, 3.1)	SAn(0.31, 0.31)	Py. (10)	100	24	0.53	0.56
7	3 (0.5, 3.1)	SAn(0.93, 0.93)	Py. (15)	100	24	0.85	1.60
8	4 (1.0, 6.2)	SAn(1.85, 1.85)	Py. (15)	100	24	1.37	1.12
9	4 (1.0, 6.2)	SAn(1.85, 1.85)	Py. (15)	100	36	1.38	1.29
10	4 (1.0, 6.2)	SAn(1.85, 1.85)	Tol. (15)	100	48	1.18	0.37
11	1 (0.5, 3.1)	MAn(0.91, 0.93)	Py. (10)	100	24	0.46	1.22
12	2 (0.5, 3.1)	MAn(0.91, 0.93)	Py. (10)	100	24	0.57	0.85
13	2 (0.5, 3.1)	MAn(4.7, 4.7)	DMAc (25) ^e	80	24	0.36	1.22
14	3 (0.5, 3.1)	MAn(0.91, 0.93)	Py. (15)	100	24	0.80	1.37
15	4 (1.0, 6.2)	MAn(1.82, 1.85)	Py. (15)	100	48	1.44	0.75
16	4 (1.0, 6.2)	MAn(1.82, 1.85)	Tol. (10)	100	72	0.98	0.29

^a mmonomol, mol glucose units.

^b Py., pyridine; Tol., toluene.

^c Degree of substitution determined by IR spectra.

^d Lithium chloride/Pulp = 1.5/1 (g/g).

substituents spreads the distance between cellulose molecules and decreases the crystallinity.

Although the crystallinity slightly decreased and the solubility increased by the substitution, no PSAs and PMAs exhibited a T_g or a T_m from the DSC measurements. This suggests that the crystallinity decreased by the steric hindrance of succinyl groups or maleyl groups, but hydrogen bonds between the cellulose molecules cannot decrease much because the

terminals of succinyl and maleyl groups are carboxyl ones.

Syntheses and properties of Pulp-g-PCL

In bulk

The reaction conditions, yield, amount of the introduction of CL unit on the cellulose, and T_g 's are shown in Table III. In the absence of a catalyst, CL units were not introduced into cellulose, while in the presence of di-*n*-butyltin dilaurate (DBTDL), CL units were introduced.

When P4SA (DS = 1.29) was used as the cellulose material, the amount of the introduction of CL was high. But when using P4MA (DS = 0.29), the amount of the introduction of CL was not too high. This may

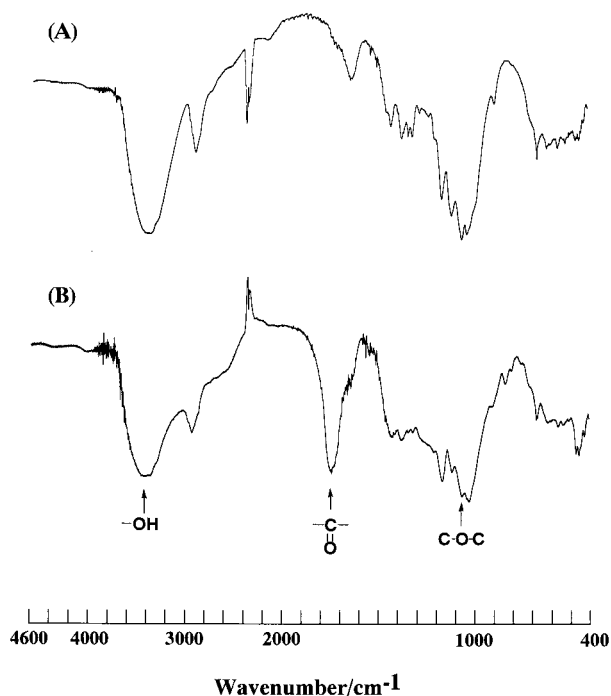


Figure 2 IR spectra of (A) Pulp4 and (B) P4SA (DS = 1.29).

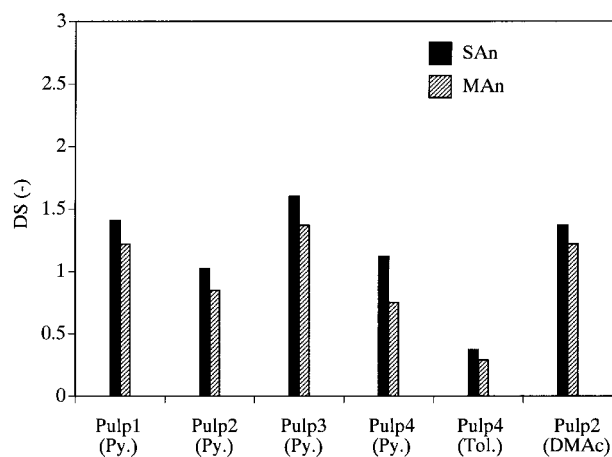


Figure 3 DS values of PSAs and PMAs.

TABLE II
Solubility of Pulp4 and P4SA

Solvent	Pulp4	P4SA (DS = 0.37)	P4SA (DS = 1.29)
Methanol	×	×	Δ
Acetone	×	×	Δ
Ethyl acetate	×	×	×
<i>n</i> -Hexane	×	×	×
Chloroform	×	Δ	Δ
Toluene	×	Δ	Δ
THF	×	Δ	Δ
Pyridine	Δ	Δ	Δ
DMAc/LiCl	Δ	Δ	○
3N NaOHaq	Δ (50.5) ^a	Δ (71.1) ^a	Δ (84.0) ^a

○, soluble; ×, insoluble; Δ, partially soluble or swelling.

^a The percentage of the soluble part is shown in parentheses.

be due to the difference between their intermolecular interactions.

The DSC curve of P4SA-g-PCL (Table III, run 7) shown in Figure 4 exhibited a T_g at the top of the peak of 72.3°C, but no melting points. Because P4SA had no T_g , the appearance of T_g may be attributed to the introduction of CL units. Because only P4SA-g-PCL and P4MA-g-PCL have T_g 's, steric effects of succinyl and maleyl groups also influenced the thermal property of the graft copolymers.

P4SA-g-PCL (Table III, run 7) was pressed at 150°C and room temperature. The pellet pressed at 150°C became transparent, while the pellet pressed at room temperature showed no transparency. XRD diagrams of these pellets are shown in Figure 5. As shown in Figure 5(A), P4SA-g-PCL exhibited a decrease of the crystallinity, compared with P4SA [Fig. 2 (B)]. It is evident that the T_g of P4SA-g-PCL appeared because of the decrease of the crystallinity. As shown in Figure

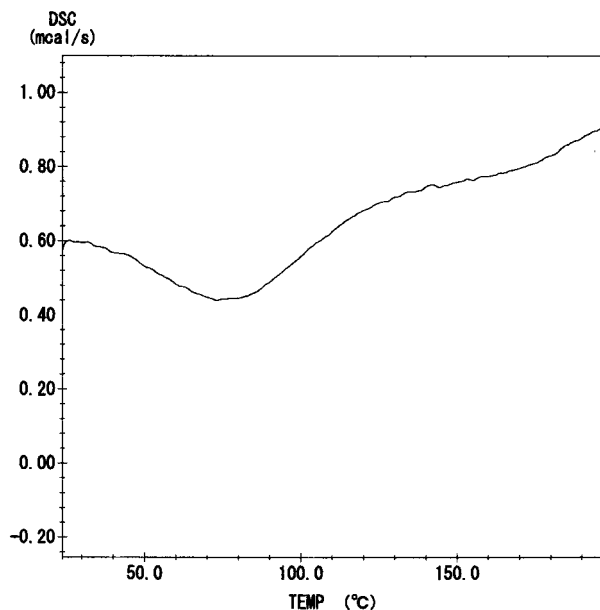


Figure 4 DSC curve of P4SA-g-PCL obtained in bulk (first scan). Heating from 20 to 200°C at a heating rate of 5°C min⁻¹.

5(B), sharp peaks appeared around $2\theta = 9.5^\circ$, 17.0° , and 28.5° . The peaks around 9.5° and 28.5° were also observed in the XRD diagrams of Pulp4 and P4SA. But the peak around 17.0° did not appear. There are no peaks around 17.0° in the XRD diagrams of the crystal structures called cellulose I and cellulose II.¹⁵ The peak at 17.0° did not exist in the XRD diagrams of PCL. Therefore, new crystal structure parts may appear in the graft copolymer by the introduction of CL units; the appearance of new peaks in Figure 5(B) was due to the reorganization of grafted-CL chains by heat molding.

TABLE III
Syntheses of Pulp-g-PCL in Bulk

Run	Pulp ^a (g)	CL (mL)	Catalyst (g)	Temperature (°C)	Time (h)	Yield (g)	CL Unit ^b (wt %)	T_g^c (°C)
1	Pulp4 (1.5)	20	—	110	48	1.48	—	—
2	Pulp4 (2.0)	20	Sn-oct (0.3)	110	24	2.03	3.15	—
3	Pulp4 (2.0)	20	Sn-oct (0.3)	150	24	2.12	5.77	—
4	Pulp4 (2.0)	20	Sn-oct (0.3)	170	12	2.03	4.56	—
5	Pulp3 (2.0)	20	Sn-oct (0.3)	110	24	2.06	4.31	—
6	Pulp3 (2.0)	20	Sn-oct (0.3)	150	24	1.94	1.73	—
7	P4SA (2.0)	20	Sn-oct (0.3)	150	24	2.24	12.82	72.3
8	Pulp4 (2.0)	20	DBTDL (0.3)	110	24	2.06	3.68	—
9	Pulp4 (2.0)	20	DBTDL (0.3)	110	72	1.98	1.90	—
10	Pulp4 (2.0)	20	DBTDL (0.3)	150	24	2.02	4.99	—
11	Pulp4 (2.0)	20	DBTDL (0.3)	150	72	2.04	6.91	—
12	P4SA (2.0)	20	DBTDL (0.3)	110	24	2.27	13.84	78.0
13	P4MA (2.0)	20	DBTDL (0.3)	150	24	2.12	5.49	75.3

^a P4SA, DS = 1.29; P4MA, DS = 0.29.

^b Amount of reacted CL determined by IR spectra.

^c Determined by DSC.

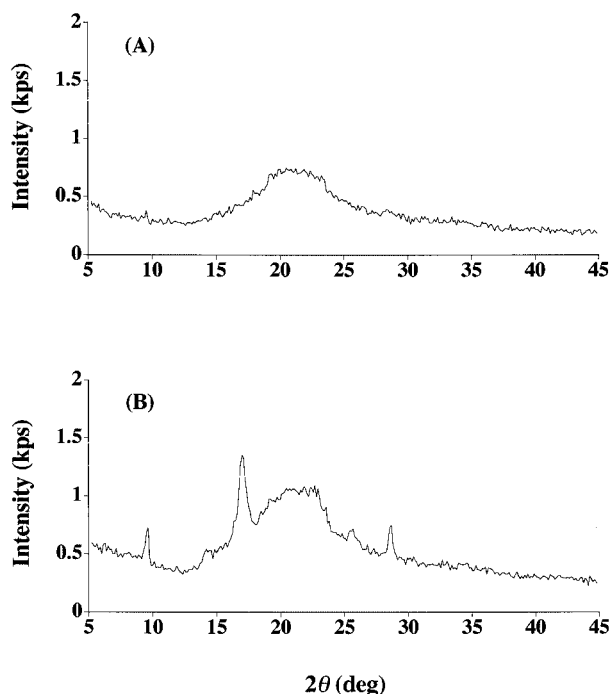


Figure 5 X-ray diffraction diagrams for press-molded pellets from P4SA-g-PCL obtained in bulk; (A) pressed at room temperature; (B) at 150°C.

In solution

The reaction conditions, yield, amount of the introduction of the CL unit on cellulose, and T_g 's are shown in Table IV. The reactions proceeded heterogeneously throughout except in the case of P4SA. The reactivity of cellulosic materials in DMAc/LiCl was not much different from that in the bulk. Although the amount of CL used in the reaction was less than in the bulk, some products obtained in DMAc/LiCl exhibited a higher amount of the introduction than that in the bulk. When MC (Table IV, run 3), which was soluble in DMAc/LiCl, was used, the amount of the introduction was higher than that for Pulp4 (Table IV, run 2). Thus, the solubility of cellulose materials in DMAc/LiCl influenced the amount of the introduction. When

the amount of DMAc increased (Table IV, run 4), the amount of the introduction decreased. Therefore, the amount of the solvent desired was as little as possible.

From the results of the DSC measurement, these products exhibited an endothermic peak, that is, a T_g , except for products of runs 1 and 4 in Table IV. The temperatures of these peaks were 90–110°C.

The amounts of the introduction of CL units in the graft copolymers obtained in DMAc/LiCl were similar to those in the bulk, but the T_g was higher. This may result from the difference of the introduction sites on cellulose between both conditions (in DMAc/LiCl and in the bulk). In the bulk, unreacted CLs preferentially reacted with terminal hydroxyl groups of the introduced CL units because of the steric hindrance of cellulose. While cellulosic materials were partially soluble in DMAc/LiCl, unreacted CLs reacted more easily with hydroxyl groups on glucose units, compared to in the bulk. Consequently, CL was introduced into several sites on glucose units, and the degree of polymerization of CL units in the bulk may be higher than that in DMAc/LiCl. Hence, the T_g 's of the graft copolymers obtained in the bulk were relatively lower than those in DMAc/LiCl.

P4SA-g-PCL (Table IV, run 6) was pressed at 150°C and room temperature. These pellets were similar to those obtained from P4SA-g-PCL (Table III, run 7), and the XRD diagrams exhibited similar peaks to those shown in Figure 5. However, the peak intensity around 17.0° was smaller than that of Figure 5(B), indicating that the peak intensity around 17.0° increases with the degree of polymerization of CL.

CONCLUSIONS

1. Chemical-modified pulps were synthesized from SAN or MAN using four types of waste pulps.
2. The solubility of the modified pulp increased with its DS. However, neither the T_g or T_m of these modified pulps was confirmed from the DSC.

TABLE IV
Syntheses of Pulp-g-PCL in DMAc/LiCl

Run	Pulp ^a (g)	CL (mL)	LiCl (g)	DMAc (mL)	Temperature (°C)	Time (h)	Yield (g)	CL unit ^b (wt %)	T_g^c (°C)
1	Pulp4 (1.0)	6	0.08	10	110	12	0.98	3.32	—
2	Pulp4 (1.0)	6	0.08	10	150	24	1.06	8.27	—
3	M.C. (1.0)	6	0.08	10	150	24	1.06	8.86	—
4	M.C. (1.0)	6	0.08	15	150	24	1.02	3.70	—
5	Pulp4 (1.0)	6	1.50	30	100	24	1.07	7.25	105.0
6	P4SA (1.0)	6	1.50	30	100	24	1.11	11.36	111.1
7	P4MA (1.0)	6	1.50	30	100	24	1.04	6.09	94.0

^a P4SA, DS = 1.29; P4MA, DS = 0.29.

^b Amount of reacted CL determined by IR spectra.

^c Determined by DSC.

3. Pulps or modified pulps were graft polymerized with CL in the bulk and in DMAc/LiCl.
4. In the bulk, the graft copolymers obtained from the modified pulps showed a T_g of about 75°C, but the graft copolymers obtained from non-modified pulps showed no T_g .
5. In DMAc/LiCl, the obtained graft copolymers from both modified and nonmodified pulps exhibited a T_g of 95–110°C.

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