

Syntheses and Biodegradability of Benzylated Waste Pulps and Graft Copolymers from PBzs and L-Lactic Acid

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ABSTRACT: Benzylated waste pulps (PBzs) were synthesized from treated waste pulp (Pulp), and benzyl chloride with phase transfer catalyst (PTC), and graft copolymers (PBz-g-LA) were synthesized from PBzs and L-lactic acid (LA). Thermal properties, solubility, crystallinity, and biodegradability of the obtained PBzs and graft copolymers were investigated. PBzs with the degree of substitution (DS) higher than 1.5 showed T_g and T_m in DSC measurement. All PBz-g-LA exhibited no T_m . However, the graft copolymers obtained from lower DS PBzs having no T_g , exhibited T_g . The solubility of PBzs enhanced with increasing DS, and the crystallinity of PBzs reduced with increasing DS because of hydrophobicity and steric effect of benzyl groups. The sol-

ubility of graft copolymers was similar to that of original PBzs. Biodegradation tests for PBzs, Pulp, and graft copolymers were performed using cellulase in 0.1 M acetate buffer solution (pH 5.5) at 37°C. All samples showed biodegradability though the biodegradation rate decreased with increasing DS of PBz. In PBz-g-LA, the initial biodegradation rate was faster than that of original PBz because of hydrolysis of LA units. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2658–2664, 2004

Key words: polysaccharides; waste; modification; graft copolymers; degradation

INTRODUCTION

Plastics made from petroleum are vital for our life because of those lightness, good processibility, good mechanical properties, and so on. However, these plastics are hardly degraded by bacteria or light when these are disposed because of its stability. Therefore, disposal of waste plastics is considered to be one of the reasons for environmental pollution. Development of biodegradable plastics is one of the measures against environmental pollution problem by waste plastics. Biodegradable plastics are defined as "a plastic that can be degraded to low molecular weight by bacteria in nature."¹ Poly(hydroxybutyrate-co-valerate) (PHBV),² poly(lactic acid) (PLA)^{3,4} and poly(ϵ -caprolactone) (PCL)^{5,6} have ever been synthesized and commercialized as biodegradable plastics. Many developments of the biodegradable plastics derived from natural polysaccharide such as cellulose derivatives^{7–10} or amylose derivatives¹¹ also have been studied.

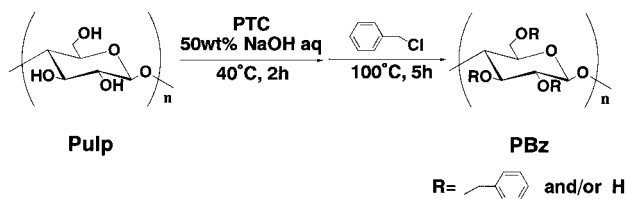
We have focused on waste pulp for cellulosic material to develop biodegradable plastics. Waste pulp is short

fibril cellulose produced from the paper manufactures. Waste pulp has been generally disposed by burning or burying. If biodegradable materials are easily prepared from waste pulp, the amount of CO₂ on burning will be reduced as well as the production cost can be down.

L-Lactic acid (LA) is a starting material for synthesis of PLA. Recently, LA is available at cheap because LA can be obtained by fermentation of starch.¹² Previously, we synthesized graft copolymers from waste pulp and LA. However, the DSC measurement for copolymers exhibited neither T_g nor T_m before thermal decomposition because of strong intermolecular hydrogen bonds. To decrease the intermolecular hydrogen bonds, we focus benzylation of waste pulp. Shiraishi et al. achieved benzylation of wood, and reported its formability and biodegradability.¹³ However, because a lignin component in wood is removed on cooking in pulping process, properties of waste pulp are essentially different from wood. In addition, the relationship between synthetic conditions of benzyl cellulose and its degree of substitution (DS) was reported previously,¹⁴ but biodegradability of it has not been reported yet.

In this article, we synthesized benzylated waste pulps (PBzs) from treated waste pulp (Pulp) and benzyl chloride with tetramethylammonium iodide as a phase transfer catalyst (PTC). The obtained PBzs bearing different degrees of substitution (DS) were graft

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Scheme 1

copolymerized with LA by the direct polycondensation method. Biodegradability of the PBzs and graft copolymers were also discussed.

EXPERIMENTAL

Purification of waste pulp

Purified pulp (Pulp) was obtained as follows: original waste pulp was refluxed in water for 3 h and filtered. The obtained fibril pulp was refluxed in 2 N HCl aq. solution for 3 h and filtered. This solid was washed thoroughly with water, filtered, and dried *in vacuo*.

Syntheses of benzylated pulps (PBzs) (Scheme 1)

Typical synthetic procedure was as follows: Pulp 5.0 g (31 mmol/glucose unit), 50 wt % NaOH aq. solution 15 mL and tetramethylammonium iodide 0.2 g (1 mmol) were added to a four-neck flask and stirred at 40°C for 2 h under nitrogen atmosphere. Then, benzyl chloride 23.6 mL (0.21 mol) was added dropwise and stirred at 100°C for 5 h under nitrogen atmosphere. After the reaction, the flask was cooled in an ice bath, and 50 mL of diethylether was added to the flask and stirred. The flask was allowed to stand for a constant time, then the supernatant solution in the flask was decanted. Further, 50 mL of diethylether was added and stirred, and then the precipitate, benzyl cellulose, was isolated by filtration. The product was washed with water, and dried *in vacuo*.

Syntheses of graft copolymers from PBzs and LA (PBz-g-LA) (Scheme 2)

Typical synthetic procedure was as follows: PBz 1.0 g (DS = 0, 6.2 mmol/glucose unit), LA 10 mL (1.2

$\times 10^{-2}$ mol) and toluene 15 mL were placed in a pear-shape flask equipped with a Dean-Stark trap, and stirred at 120°C for 24 h. After reaction, the product was poured into methanol and filtered under vacuum. Further, the product was washed thoroughly with methanol and dried *in vacuo*.

Biodegradation test

Molding of test piece

Fifty milligrams of PBz were placed in a tablet molder and heated at 200°C for 1.5 h. The molder was pressed at 200 kg/cm² for 0.5 h with keeping the temperature, and then cooled to room temperature with keeping the pressure.

Preparation of enzyme solution

Acetic acid (2.86 mL, 0.05 mol) and 23.05 g of sodium acetate (0.05 mol) were placed in a 500 mL mess flask, and 200 mL of distilled water was added. After being completely dissolved, distilled water was added until total volume became 500 mL to give 0.1 M acetate buffer (pH 5.5).

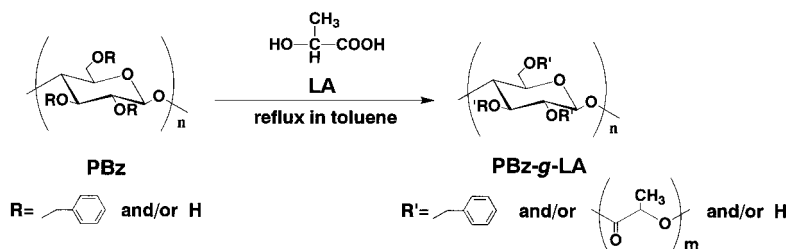
Cellulase AP (0.1 g) was placed in a 100-mL mess flask and 50 mL of acetate buffer was added. After cellulase was completely dissolved, acetic acid buffer was added until total volume became 100 mL, to give 0.1% cellulase solution.

Biodegradation test of PBzs and PBz-g-LA

A press-molded pellet of PBz (approximately 50 mg, diameter of 1.3 cm, 350 μm thickness) was placed in a test tube containing 5 mL of 0.1% cellulase solution. The test tube was incubated at 37°C and shaken for the required days. After incubation, the pellet was washed with water and dried *in vacuo*. Then the weight loss of the pellet was measured to evaluate the degradation.

Measurement

IR spectrum was taken on an FTIR-8100A (Shimadzu) spectrometer by KBr disk. X-ray diffraction was mea-



Scheme 2

TABLE I
Syntheses of Benzylated Pulps using $(\text{CH}_3)_4\text{NI}$

Run	Pulp (g)	BzCl (mL)	NaOHaq ^a (mL)	Catalyst (mmol)	Temp. (°C)	Time (h)	T_g^b (°C)	T_m^b (°C)	DS ^c (—)
1	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	80	10	— ^d	— ^d	— ^d
2	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (0.5)	100	5	— ^d	— ^d	— ^d
3	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (0.75)	100	5	— ^d	— ^d	0.49
4	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	3	— ^d	— ^d	1.11
5	5.0	5.9	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	5	— ^d	— ^d	0.83
6	5.0	11.8	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	5	160.2–179.7	218.6	1.50
7	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	5	162.7–166.9	199.2	1.78
8	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	15	158.4–167.2	233.2	2.50
9	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	100	24	154.9–162.2	195.2	2.53
10	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.25)	100	5	138.6–143.1	177.4	1.61
11	5.0	23.6	20	$(\text{CH}_3)_4\text{NI}$ (1.0)	120	5	154.6–170.5	192.2	1.84

^a Concentration; 50 wt %.

^b Determined from DSC measurement.

^c DS (degree of substitution) was calculated from peak intensity ratio on IR spectra ($A_{(3030\text{ cm}^{-1})}/A_{(2900\text{ cm}^{-1})}$).

^d Not determined.

sured with an X-ray diffractometer XR-D1 (Shimadzu). DSC measurement of products was accomplished on a DSC 3100 equipped with MTC 1000S (MAC science). Melting point was measured with a METTLER FP82HT Hot Stage equipped with a Mettler FP80HT Central Processor (Mettler) and Olympus Model PM-10-M (Olympus) apparatus. Press molding of graft copolymers was performed using a Yuatu Power P-1-B (Riken Seiki) and a Tablet Molder (JASCO) apparatus.

Reagents

Solvents for all reactions were purified by a general procedure. Waste pulp was supplied by Murakami Shoji Co. Ltd. Tetramethylammonium iodide and tetraethylammonium chloride were purchased from Tokyo-Kasei Industry and used without purification. Tetramethylammonium chloride was purchased from Wako chemical Co. Ltd. and used without purification. Tetra-*n*-butylammonium bromide was purchased from Ishizu Seiyaku Co. Ltd. and used without purification. Cellulase AP was purchased from Amano Seiyaku Co. Ltd.

RESULTS AND DISCUSSION

Syntheses of PBzs

Table I shows the results of syntheses of benzylated pulps using $(\text{CH}_3)_4\text{NI}$. DSs were estimated on the basis of a calibration curve shown in Figure 1 calculated from the peak intensity ratio between a peak around 3030 cm^{-1} due to phenyl groups and a peak around 2900 cm^{-1} due to C—H stretching vibration in glucose units. All PBzs bearing the DS value more than 1.5 were exhibited T_g and T_m . In Table I, it is

found that the conditions of 1 mmol of catalyst to 5 g of Pulp were the optimum amount.

Reaction conditions and results of syntheses of PBz using $(\text{CH}_3)_4\text{NCl}$, $(\text{C}_2\text{H}_5)_4\text{NCl}$, and $(n\text{-C}_4\text{H}_9)_4\text{NBr}$ as PTC are shown in Table II. DS values of PBzs were different according to types of PTC. In $(\text{C}_2\text{H}_5)_4\text{NCl}$, the obtained PBz exhibited higher DS value even with the smallest amount of PTC. Thermal properties of PBz were similar to that in Table I, that is, all PBz having the DS value more than 1.5 exhibited T_g and T_m in the DSC measurement.

Solubility of PBz bearing DS of 0.83, 1.78, and 2.53 (runs 5, 7, and 9 in Table I) and Pulp are shown in Table III. The solubility of PBzs in organic solvents increased with increasing DS. XRD diagrams of PBzs bearing DS of 0, 1.78, and Pulp are shown in Figure 2. It was found that crystallinity of PBz [Fig. 2(B)] decreased compared with that of Pulp [Fig. 2(A)], despite the fact that no benzyl groups were introduced in

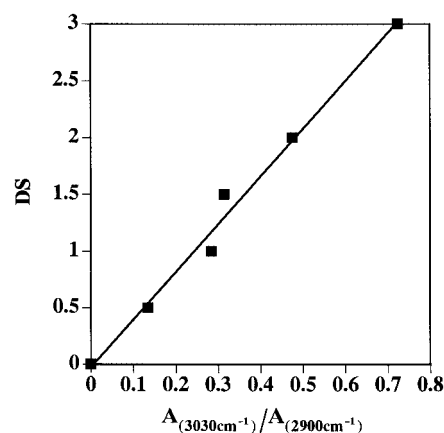


Figure 1 Relationship between the DS of PBz and the ratio of absorbance for IR spectra.

TABLE II
Syntheses of Benzylated Pulps Using other PTC

Run	Pulp (g)	BzCl (mL)	NaOHaq ^a (mL)	Catalyst (mmol)	Temp. (°C)	Time (h)	T_g^b (°C)	T_m^b (°C)	DS ^c (-)
1	5.0	23.6	20	(CH ₃) ₄ NCI (0.5)	100	5	147.7–150.8	179.4	0.91
2	5.0	23.6	20	(CH ₃) ₄ NCI (1.0)	100	5	156.6–171.5	193.1	1.41
3	5.0	23.6	20	(CH ₃) ₄ NCI (1.5)	100	5	164.2–170.4	182.2	1.96
4	5.0	23.6	20	(CH ₃) ₄ NCI (2.0)	100	5	161.8–168.1	218.9	2.14
5	5.0	23.6	20	(CH ₃) ₄ NCI (2.5)	100	5	151.8–164.1	198.6	2.27
6	5.0	23.6	20	(CH ₃) ₄ NCI (3.0)	100	5	160.3–167.0	190.6	2.28
7	5.0	23.6	20	(CH ₃) ₄ NCI (3.5)	100	5	152.2–159.6	201.0	1.77
8	5.0	23.6	20	(CH ₃) ₄ NCI (1.0)	100	24	174.8–179.1	192.8	2.37
9	5.0	23.6	20	(C ₂ H ₅) ₄ NCI (0.25)	100	5	155.9–163.2	177.5	1.78
10	5.0	23.6	20	(C ₂ H ₅) ₄ NCI (0.5)	100	5	137.4–147.9	161.7	2.15
11	5.0	23.6	20	(C ₂ H ₅) ₄ NCI (1.0)	100	5	120.2–124.1	152.4	1.49
12	5.0	23.6	20	(C ₂ H ₅) ₄ NCI (1.5)	100	5	— ^d	— ^d	0.37
13	5.0	23.6	20	(C ₂ H ₅) ₄ NCI (1.0)	100	24	166.3–170.7	204.2	2.30
14	5.0	23.6	20	(<i>n</i> -Bu) ₄ NBr (0.5)	100	5	— ^d	— ^d	— ^d
15	5.0	23.6	20	(<i>n</i> -Bu) ₄ NBr (1.0)	100	5	— ^d	— ^d	— ^d
16	5.0	23.6	20	(<i>n</i> -Bu) ₄ NBr (1.0)	100	24	— ^d	— ^d	— ^d

^a Concentration; 50 wt %.

^b Determined from DSC measurement.

^c DS (degree of substitution) was calculated from peak intensity ratio on IR spectra ($A_{(3030\text{ cm}^{-1})}/A_{(2900\text{ cm}^{-1})}$).

^d Not determined.

PBz [Fig. 2(B)]. This indicated that the crystallinity of Pulp was changed by swelling in NaOH aq. solution. In Figure 2, the crystallinity of PBzs decreased with increasing DS. This was caused by enhancement of hydrogen bond power and the steric effect of bulky benzyl groups. This also contributed to the result in Table III.

Syntheses of PBz-g-LA

Reaction conditions, yield, T_g and LA contents in graft copolymers, were shown in Table IV. PBzs bearing four types of DS were used. LA contents were calculated, according to a calibration curve prepared from the peak intensity ratio between a peak around 1750 cm^{-1} assigned to carbonyl groups and a peak around 1050 cm^{-1} due to ether bonds in the glucose unit. The calibration curve is shown in Figure 3. No graft copol-

TABLE III
Solubility^a of PBz^b Bearing Several DS

Solvent	DS = 0.83	DS = 1.78	DS = 2.53	Pulp
Methanol	×	×	×	×
Acetone	×	×	△	×
Ethyl acetate	×	△	△	×
<i>n</i> -Hexane	×	×	×	×
Chloroform	△	○	○	×
Toluene	△	○	○	×
THF	×	○	○	×
DMSO	×	△	△	×

^a ○, soluble; ×, insoluble; △, partially soluble or swelling.

^b Prepared in the presence of (CH₃)₄NI.

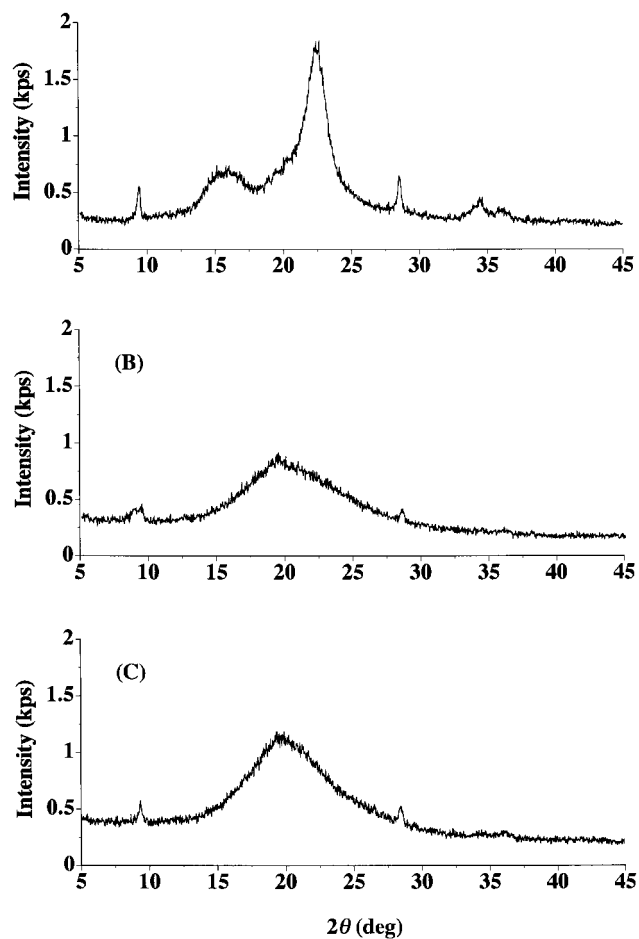


Figure 2

Figure 2 X-ray diffraction diagrams for (A) pulp, (B) PBz (DS = 0), and (C) PBz (DS = 1.78).

TABLE IV
Syntheses of Graftcopolymers from PBz and L-Lactic Acid (LA) in Reflux^a

Run	PBz (DS)	LLA (mL)	Solvent ^b (mL)	Catalyst ^c (wt %)	Yield (%)	T_g^d (°C)	LA contents ^e (wt %)
1	PBz (0)	1.0	Tol. (15)	—	73.9	— ^f	10.9
2	PBz (0)	1.0	Tol. (15)	<i>p</i> TS (25)	74.3	186.9	7.18
3	PBz (0.83)	1.0	Tol. (15)	—	80.3	198.6	12.7
4	PBz (0.83)	1.0	Tol. (15)	<i>p</i> TS (25)	89.1	176.7	10.9
5	PBz (0.83)	1.0	Xyl. (15)	—	78.7	187.5	9.55
6	PBz (0.83)	1.0	Xyl. (15)	<i>p</i> TS (25)	85.7	195.4	8.87
7	PBz (1.78)	1.0	Tol. (5)	—	86.8	153.0	4.58
8	PBz (1.78)	1.0	Tol. (15)	—	88.0	172.1	7.37
9	PBz (1.78)	1.0	Tol. (15)	<i>p</i> TS (25)	87.6	175.4	5.77
10	PBz (2.53)	1.0	Tol. (15)	—	85.7	171.1	3.71
11	PBz (2.53)	1.0	Tol. (15)	<i>p</i> TS (25)	73.8	170.6	2.95

^a 1.0g of PBz was used, reaction time; 24 h.

^b Tol.; toluene, Xyl.; xylene.

^c *p*TS; *p*-toluenesulfonic acid.

^d Determined from DSC measurement.

^e Calculated from peak intensity ratio on IR spectra ($A_{(1750\text{ cm}^{-1})}/A_{(1050\text{ cm}^{-1})}$).

^f Not determined.

ymers exhibited T_m . Graft copolymers obtained from PBzs with higher DS exhibited lower LA contents than those obtained from PBzs with lower DS. This is caused that hydroxyl groups on the 6-position of glucose units in high-DS PBzs having higher reactivity than other positions were already substituted by benzyl groups. When DS of PBzs was very low, for example, approximately 0, LA contents in graft copolymer was low because low-DS PBzs were not soluble in toluene. As a result, the optimum DS of PBz was approximately 1 in this reaction. T_g of the graft copolymers increased with the LA contents. This may result from the fact that hydrogen bond power of the graft copolymer increases because of the LA units introduced in PBz behavior as spacers.

The solubility of graft copolymers was hardly different from original PBz used as starting material,

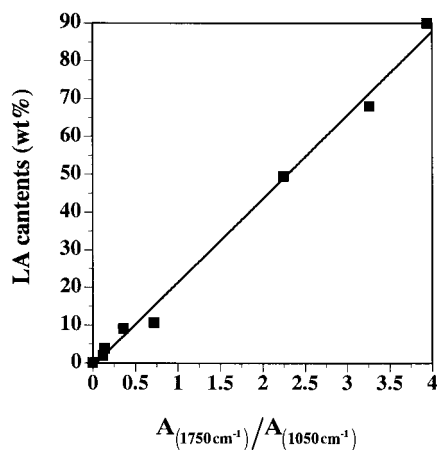


Figure 3 Relationship between the LA contents in graft copolymer and the ratio of absorbance for IR spectra.

while the crystallinity of graft copolymers slightly increased. XRD diagrams of PBz (DS = 0.83) and PBz-g-LA (DS = 0.83, LA contents = 12.7 wt %, in Table IV, run 3) are shown in Figure 4. The slightly enhanced crystallinity for PBz-g-LA is due to the increase of hydrogen bond power by PLA.

Biodegradability of PBzs

The results of biodegradation test for PBzs pellets bearing DS of 0.83, 1.78, 2.53 (runs 5, 7, and 9 in Table

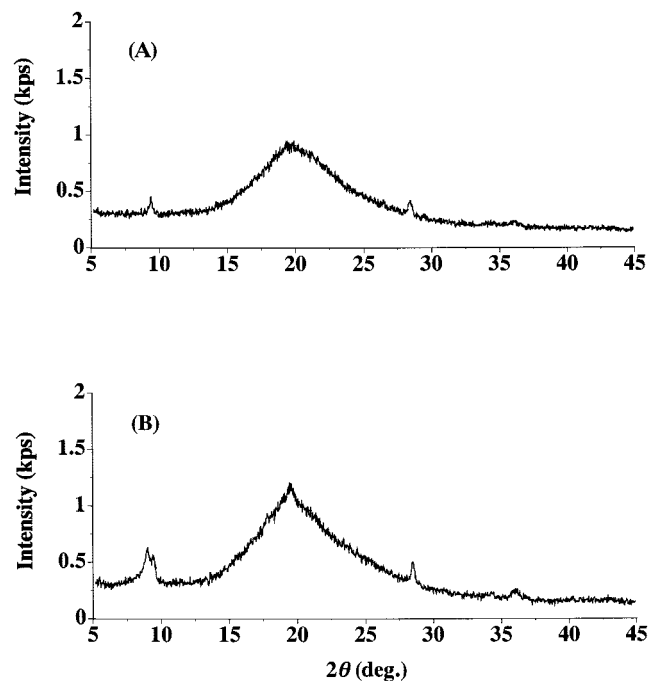


Figure 4 X-ray diffraction diagrams for (A) PBz (DS = 0.83) and (B) PBz-g-LA (LA contents = 12.7 wt %).

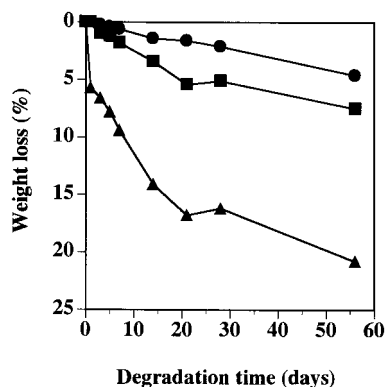


Figure 5 Biodegradation test of benzyl cellulose pellets in enzyme solution. (▲) DS = 0.83, (■) DS = 1.78, and (●) DS = 2.53.

I) are shown in Figure 5, and those for PBzs powder and Pulp are shown in Figure 6. All PBzs exhibited biodegradability though the weight loss decreased with increasing DS. This result may be caused by the fact that hydrolysis on β -glycoside bonds in main chain was prevented from steric hindrance and high hydrophobicity of substituent. Because biodegradability was confirmed even for the pellet of high-DS-PBz, it is expected that all PBzs are completely degraded to low molecular weight finally. The powder samples showed higher biodegradability than pellet samples. This is attributed to the difference of the surface area of samples per a unit weight or difference of crystallinity. The contact area of samples with water becomes large with increasing surface area, and water easily permeates into samples with decreasing crystallinity. Therefore, the hydrolysis rate of samples rises with increasing the surface area per a unit weight and decreasing crystallinity.

The change of DS of PBzs after biodegradation test is shown in Figure 7. DS changes of PBzs bearing DS of 0.83 and 2.53 were hardly observed, while that of

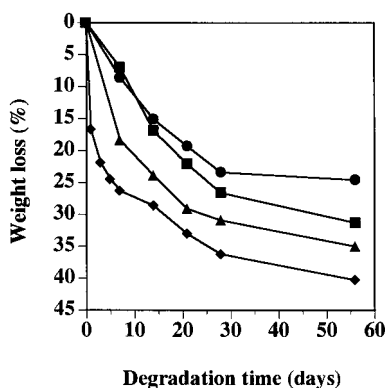


Figure 6 Biodegradation test of benzyl cellulose powder and Pulp powder in enzyme solution. (▲) DS = 0.83, (■) DS = 1.78, (●) DS = 2.53, and (◆) Pulp.

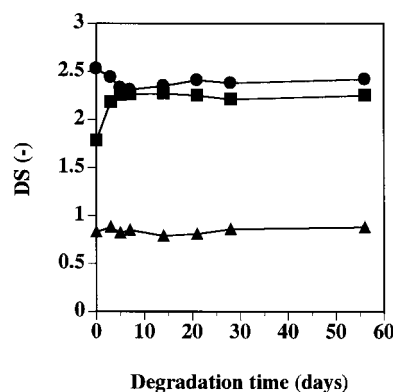


Figure 7 Plots of DS of PBz vs. degradation time. (▲) DS = 0.83, (■) DS = 1.78, and (●) DS = 2.53.

PBz bearing DS of 1.78 was remarkable at the initial biodegradation period. This result indicated that hydrolysis on β -glycoside bonds around non-, or mono-substituted glucose units occurred more easily than around di-, or tri-substituted ones. This is in fair agreement with the experimental results in Figures 5 and 6.

Biodegradability of PBz-g-LA

Results of biodegradation test of PBz-g-LA pellet (runs 3, 8, and 10 in Table IV) and powder (runs 1, 3, 8, and 10 in Table IV) are shown in Figures 8 and 9. Because the graft copolymer obtained from PBz having DS of 0 could not be molded, this sample was investigated only in powder. On the whole, the initial weight loss of graft copolymers was larger than that of the original PBz. This may be caused by hydrolysis of LA units in acidic solution. Tendency of biodegradability of graft copolymers was similar to that of original PBz, that is, the biodegradation rate of graft copolymers was dependent on the DS of PBz, and reduced with increasing DS of PBz.

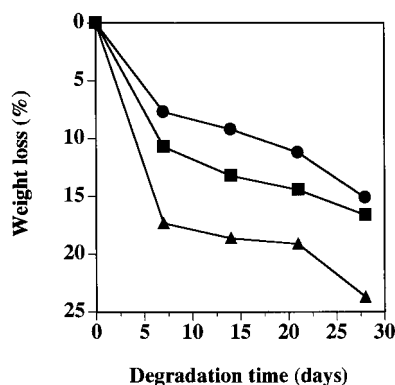


Figure 8 Biodegradation test of PBz-g-LA pellets in enzyme solution. (▲) PBz (DS = 0.83), LA contents = 12.7 wt %, (■) PBz (DS = 1.78), LA contents = 7.37 wt %, and (●) PBz (DS = 2.53), LA contents = 3.71 wt %.

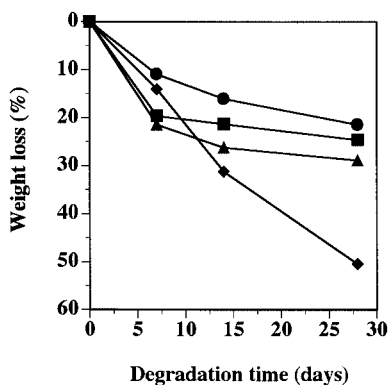


Figure 9 Biodegradation test of PBz-g-LA powders in enzyme solution. (◆) PBz (DS = 0), LA contents = 10.9 wt %, (▲) PBz (DS = 0.83), LA contents = 12.7 wt %, (■) PBz (DS = 1.78), LA contents = 7.37 wt %, and (●) PBz (DS = 2.53), LA contents = 3.71 wt %.

CONCLUSIONS

Benzylated waste pulps (PBzs) were synthesized from Pulp and benzyl chloride using several PTC. All PBzs with DS more than 1.5 showed T_g and T_m in DSC measurement. The solubility of PBzs rose with increasing DS, and the crystallinity of PBzs reduced with increasing DS.

Graft copolymers were synthesized from PBzs and LA (PBz-g-LA). Even when lower DS-PBzs bearing no T_g were used for a starting material, the obtained graft copolymers showed T_g in DSC measurement.

It was found that all samples of PBzs (DS = 0.83, 1.78, and 2.53), Pulp, and graft copolymers exhibited biodegradability although the biodegradation rate decreased with increasing DS of PBz. In PBz-g-LA, the initial biodegradation rate was faster than that of original PBz because of hydrolysis of LA units.

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