

Recovery and Recycle System for Chemicals in Benzylolation Process of Cellulosic Materials

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Benzylolation of cellulose and lignocellulose materials was carried out and the properties of benzylated products were investigated by FT-IR, thermal mechanical analysis (TMA), solubility test in organic solvents, moisture regain, and microscopic studies. Recovery and recycle systems for chemicals in the benzylolation process were proposed. Unreacted benzyl chloride, by-products and water were removed from reactor by vacuum / steam distillation. The distilled mixture was readily separated into two layers, hydrophobic layer and aqueous layer. The content of benzyl chloride in the hydrophobic layer was from 95 to 98%. The recovered benzyl chloride was able to be used as a reagent for benzylolation.

1. INTRODUCTION

Benzyl cellulose and benzylated lignocellulose show thermoplasticity, degradability in an activated sludge, and photo-degradability on exposure to sunlight. These materials also have a good compatibility with other polymers such as polycaprolactone and styrene [1, 2]. Good molding property and biodegradability were also found in the polyblend. The system for recovery and recycling of chemicals of benzylolation of cellulosic materials, however, have not been developed. The system will be essential for prevention of environmental pollution and for safety of operation in the industrial scale production. For these reasons recovery and recycle systems for chemicals in benzylolation process of cellulosic materials were investigated.

2. EXPERIMENTAL

2.1. Materials

Dissolving pulps (Dai-ichi Kogyo Seiyaku Co. Ltd.) and steam-exploded wood fibers were used as starting cellulosic materials. The steam-exploded wood fibers were extracted with water and 1% aqueous NaOH solution and washed with water to neutrality.

Sodium hydroxide (special grade), benzyl chloride, methanol, and tetrahydrofuran were purchased and used as reagents without further purification.

2.2. Benzylolation of dissolving pulps in flask

Dissolving pulps were treated with sodium hydroxide solution (17.5%, 25%, and 40%, 100g) at 20°C for 1 hr. The mixture was transferred into a three-neck separable flask (500 ml) and benzyl chloride (100g) was added. The flask was equipped with a condenser and a uniaxial stirrer, and then placed in an oil bath. The reaction temperature was maintained from 105 to 110°C. Benzylated product was washed with methanol and water, successively, and first dried in air and secondly by vacuum. The yield of reaction product was calculated from the weight gain.

2.3. Benzylolation of cellulosic materials in a kneader

Dissolving pulps (30g) or steam-exploded wood fibers (30g) were mixed with an aqueous 40% NaOH solution (150g or 250g) in a biaxial kneader (1000 ml) equipped with the inlet and outlet for nitrogen at room temperature for 1 hr in a nitrogen atmosphere. The kneader was, then, equipped with a condenser, and benzyl chloride was added to the mixture. The benzylolation reaction was carried out at 105°C.

2.4. Recovery of chemicals and purification of benzylated product

After benzylolation unreacted benzyl chloride, by-products (benzyl alcohol and dibenzyl ether) in the reaction mixture were recovered together with water by vacuum distillation. The benzylated product was purified by washing with water and successively with methanol.

2.5. Gas chromatographic analysis of recovered chemicals and washings

The recovered chemicals and washings were analyzed by using a gas chromatograph (Shimadu, GC-14A) which had a thermal conductivity. The separation was carried out at a column temperature from 40 to 200°C (heating rate 10°C/min), with a Thermon-3000, 5% on Shinkarbon A column using helium as the carrier gas in a flow rate of 60 ml/min.

2.6. FT-IR and thermo-mechanical analysis

FT-IR spectra from KBr pellet of benzylated cellulose were obtained on an FT-IR spectrophotometer (JASCO, FT/IR-3). Thermal properties of benzylated products were determined using a thermo-mechanical analyzer (Rigaku, Thermoflex TAS-200 system, TMA 8140C). The testing temperature ranged from room temperature to 300°C, and the heating rate was 5°C/min.

2.7. Solubility test and morphological observation

Solubility of benzyl cellulose (20mg) in various organic solvents (5ml) was determined by the appearance of solution. The surface morphology was observed using an optical microscope.

3. RESULTS and DISCUSSION

The spectra of benzyl cellulose in Figure 1 show that the substitution of benzyl ether groups to the hydroxyl groups of cellulose occurred, which is supported by the increasing intensity of the newly appearing absorption band at 3090, 3060, and 3030 cm⁻¹ (aromatic ring stretching), 1500 cm⁻¹ (aromatic C=C bond stretching), 1210 and 1370 cm⁻¹ (deformation of methylene group bonding to aromatic ring), 695 and 740 cm⁻¹ (out-of plane bending of aromatic ring), and contrary the decreasing intensity of the absorption band at about 3400 cm⁻¹ (OH stretching) with the increase of weight gain of the benzylated products.

Figure 2 shows that the softening temperature decreases with increasing in the yield of benzylated product. The softening temperature for the benzylated cellulose of 124%, 161% and

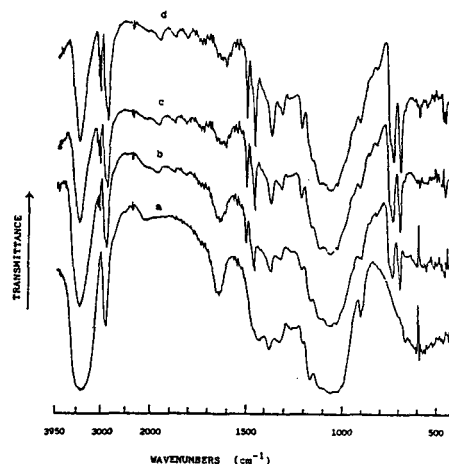


Figure 1. FT-IR spectra of benzylated cellulose. Yield: (a) control, (b) 124%, (c) 161%, (d) 175%

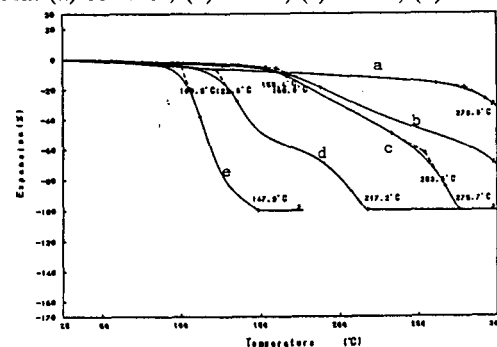


Figure 2. TMA curve of benzylated cellulose. Yield: (a) Control, (b) 124%, regenerated from MMNO · H₂O solution, (c) 124%, (d) 161%, (e) 175%

Table 1 Solubility of benzylated cellulose in various organic solvents.

Solvents	Solubility*		
	Yield of benzyl cellulose		
	124%	161%	175%
MMNO · H ₂ O**	SL	INS	INS
N,N-Dimethyl acetamide	INS	INS	SL
N,N-Dimethyl formamide	INS	INS	SL
Dimethyl sulfoxide	INS	SL	SL
1,4-Dioxane	INS	INS	INS
Tetrahydrofuran	INS	INS	SL
Benzene	INS	INS	INS
Toluene	INS	INS	INS
o-Dichlorobenzene	INS	INS	INS
Chloroform	INS	INS	INS
Diocyl phthalate	INS	INS	INS
Methyl acetate	INS	INS	INS
Acetone	INS	INS	INS
Isopropyl alcohol	INS	INS	INS

*SL:soluble,INS:insoluble,**MMNO · H₂O:NMethylmorpholine N-oxide mono-hydrate

Table 2 Benzylation conditions for dissolving pulp and resultant data for benzylated products.

Concentration of NaOH, %	Aq. alkali (g/g pulp fibers)	Benzyl chloride (g/g pulp fibers)	Yield %	Moisture content at 25°C, 65RH%
Control				6.88
17.5	5.0	5.0	124	3.74
25.0	5.0	5.0	161	1.35
40.0	5.0	5.0	175	0.92

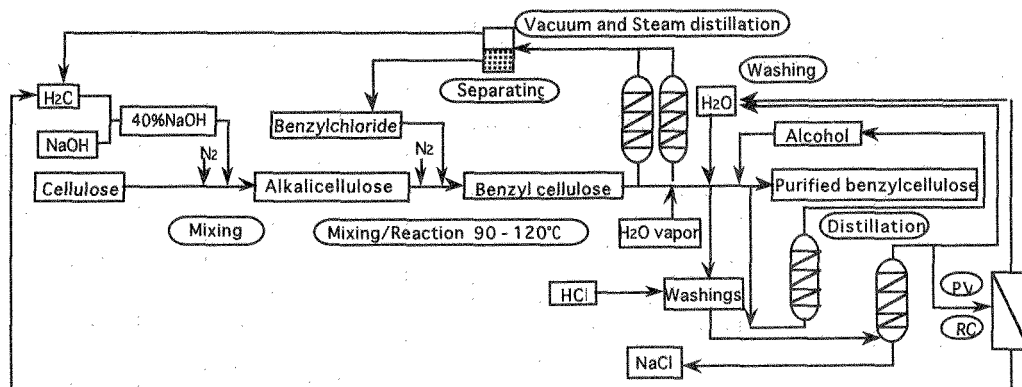


Figure 3. Recovery and recycle system for chemicals in benzylation of cellulosic materials.

PV: Pervaporation process, RO: Reverse Osmosis process.

the molten temperature are 275.7, 217.2 and 147.9°C, respectively.

Table 1 shows that the results of solubility test of benzylated cellulose in various organic solvents. The benzylated cellulose of 175% yield dissolves in N, N-dimethylacetamide, N, N-dimethylformamide, dimethyl sulfoxide and tetrahydrofuran. As shown in Table 2, moisture regain of benzylated cellulose at 25°C, 65% relative humidity decreases with increase in yield. These results support the FT-IR spectra data in Figure 1 as discussed earlier.

In the conventional benzylation process of cellulose and lignocellulosics the method for overcoming the difficulty of handling the toxic benzyl chloride has not been developed. This problem hinders the industrialization of benzylation process. It is thus important to solve the problem. The author proposes the system for recovery and recycling of chemicals in benzylation of cellulosic materials in Figure 3. Elemental technologies in this system are here investigated in the laboratory scale. Table 3 shows the results of gas chromatographic analysis of composition of chemicals recovered by vacuum distillation of the benzylation reaction mixtures. The greatest amount of the component recovered chemicals is benzyl chloride and comprises from 95 to 98%.

Table 3 Composition of chemicals recovered by vacuum distillation.

Compounds	Percentage
Benzyl chloride	95 ~ 98
Benzyl alcohol	2 ~ 4
Dibenzyl ether	< 1

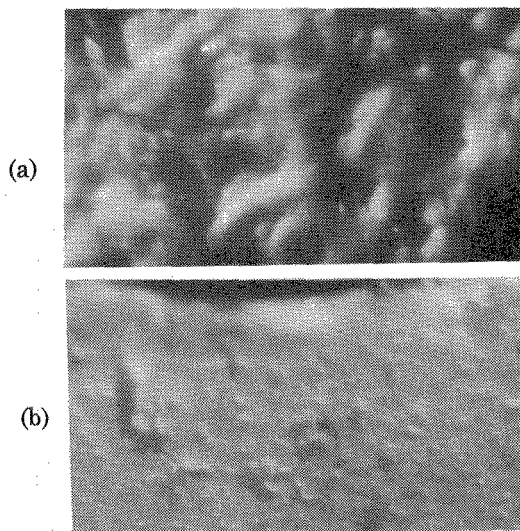


Figure 4. Microscopic appearance of benzylated cellulose, (a) surface, (b) section.

Table 4 Benzylation conditions for various cellulosic materials and resultant data for products.

Cellulosic material	40%NaOH g	Benzyl chloride g	Reaction time h	Yield %	Solubility in THF, %	Recovery of benzyl chloride, %
Dissolving pulp	250	317	4	208	99	80
"	150	317	4	214	99	67
"	250	60	4	147		4
Lignocellulose*	250	317	4	186	37	76
"	250	317	6	183	54	44
Recycled paper	250	317	4	209		52
Lignocellulose**	150	156	4	167	87	

* Hinoki wood (Japanese cypress) fiber steam-exploded (20kg/cm², 6min), Content of Klason lignin, 15.3%

** Shirakaba wood (Birch) fibers steam-exploded (20kg/cm², 6min), Content of Klason lignin, 32.9%

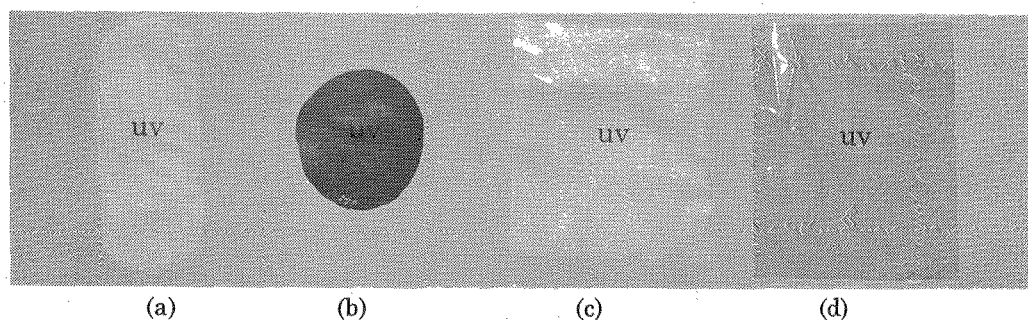


Figure 5 Benzylated cellulose and lignocellulose sheet and films. (a) Hot-pressed benzylated cellulose, (b) hot-pressed benzylated lignocellulose, (c) benzylated cellulose film prepared by casting, (d) benzylated lignocellulose film prepared by casting method.

By-products are benzyl alcohol, from 2 to 4%, and dibenzyl ether, less than 1%. The recovered chemicals are therefore able to be used for benzylation reagent.

Table 4 shows the yield of benzylated products in the kneader, solubility of the products in tetrahydrofuran, and the recovery of unreacted benzyl chloride. The yield of products in kneader is higher than that in flask shown in Table 2. It is considered that this difference is because of the difference of efficiency between biaxial and uniaxial stirring. Table 4 also shows that the solubility of benzylated lignocellulose in tetrahydrofuran is low because of the presence of lignin.

Figure 4 shows the microphotographic observation of a benzylated cellulosic material. Gush holes and porous structure which were formed by the vacuum distillation are observed on the surface (a) and the section (b), respectively. The porous structure helps the efficiency of washing and purifying the benzylated product. A hot-pressed sheet (a) of benzyl cellulose (208%

of yield) and (b) of benzylated lignocellulose (186% of yield) are shown in Figure 5. Benzyl cellulose film (c) and benzylated lignocellulose film (d) which were prepared by casting method are also shown in Figure 5. The characters of UV can be seen through the sheets and films. Very small dark spots are observed in sheet (b). These spots might be an evidence of the nonuniformity of thermal flow caused by the presence of lignin.

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