

# Preparation of Regenerated Cellulose Fiber via Carbonation.

## I. Carbonation and Dissolution in an Aqueous NaOH Solution

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**Abstract:** Cellulose carbonate was prepared by the reaction of cellulose pulp and CO<sub>2</sub> with treatment reagents, such as aqueous ZnCl<sub>2</sub> (20-40 wt%) solution, acetone or ethyl acetate, at -5-0°C and 30-40 bar (CO<sub>2</sub>) for 2 hr. Among the treatment reagents, ethyl acetate was the most effective. Cellulose carbonate was dissolved in 10% sodium hydroxide solution containing zinc oxide up to 3 wt% at -5-0°C. Intrinsic viscosities of raw cellulose and cellulose carbonate were measured with an Ubbelohde viscometer using 0.5 M cupriethylenediamine hydroxide (cuen) as a solvent at 20°C according to ASTM D1795 method. The molecular weight of cellulose was rarely changed by carbonation. Solubility of cellulose carbonate was tested by optical microscopic observation, UV absorbance and viscosity measurement. Phase diagram of cellulose carbonate was obtained by combining the results of solubility evaluation. Maximum concentration of cellulose carbonate for soluble zone was increased with increasing zinc oxide content. Cellulose carbonate solution in good soluble zone was transparent and showed the lowest absorbance and the highest viscosity. The cellulose carbonate and its solution were stable in refrigerator (-5°C and atmospheric pressure).

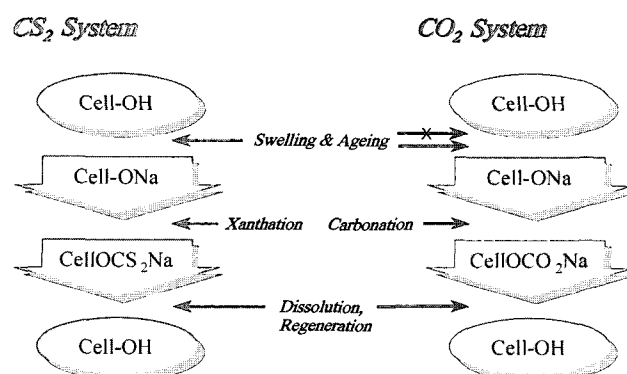
**Keywords:** Cellulose carbonate, CO<sub>2</sub>, Sodium hydroxide solution, Solubility, Phase diagram

### Introduction

Cellulose, 1,4'-O-(β-D-glucopyranoside) polymer, is one of the most abundant renewable resources on the earth[1,2]. The importance of cellulose materials has been increased since oil-crisis. However, the use of cellulose is limited because it is soluble in few solvents and also does not melt until thermal degradation because of strong intra- and inter-molecular hydrogen bonding[3]. The intrinsic insolubility of cellulose has provided considerable stimuli to prepare chemically modified celluloses. To dissolve cellulose, it is necessary that the solvent molecules diffuse into cellulose molecules and disrupt the crystallites. In cellulose derivatives, solvent can penetrate into chain molecules easily because dominant portion of hydrogen bonding is destructed.

Viscose rayon, one of regenerated celluloses and the first commercial manmade fiber, is a typical example of indirect dissolution process and is manufactured annually at a level of ca. 3,000,000 ton worldwide. The conventional viscose process uses high contents of sodium hydroxide and carbon disulfide (CS<sub>2</sub>) to break down crystalline regions of cellulose and converts cellulose into a metastable liquid called viscose[4]. The process involves the treatment of pulp with sodium hydroxide, an 'ageing' step to reduce the DP (degree of polymerization), reaction with carbon disulfide and dissolution in alkali solution. The liquid viscose is then taken into a spinning step to regenerate cellulose in a desired solid

form. Hydrogen sulfide (H<sub>2</sub>S) and by-products are also generated by reacting of carbon disulfide and H<sub>2</sub>SO<sub>4</sub> of coagulants in the spinning step and they cause occupational disease and some environmental problems[5,6]. Because environmental regulations have forced old viscose plants to close or to undergo expensive upgrades in pollution abatement equipment, related industries are investigating some methods for lower emission. One of the researches has yielded a promising result in the solvent system of amine oxide. Lyocel fiber was commercialized by using N-methylmorpholine-N-oxide (NMMO·H<sub>2</sub>O) as a direct solvent[7,8]. Other attempts such as breakdown of intra-molecular hydrogen bonding by steam explosion, electron



**Scheme 1.** Comparison of conventional CS<sub>2</sub> system and CO<sub>2</sub> system proposed in this study.

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processing or urea derivatization made cellulose soluble in an aqueous sodium hydroxide solution[9].

The objective of this research is to develop an environmentally friendly process for preparing regenerated cellulose fiber by modifying the conventional viscose process (Scheme 1). Cellulose carbonate was prepared and its solubility according to the change of carbonation and dissolution conditions was evaluated by viscosity measurement, optical microscopy and UV absorbance measurement. From the results of solubility evaluation, phase diagram of cellulose carbonate was obtained.

## Experimental

### Materials

Pulp sheet (Cellunier-F<sup>®</sup>, Rayonier Fernandina Mill, USA, DP 850, 92%  $\alpha$ -cellulose) commonly used in viscose process was shredded to the form of powders ( $\Phi$  1 mm). Commercially available compressed carbon dioxide gas was used for carbonation of cellulose. First grade reagents of zinc chloride, acetone, ethyl acetate, sodium hydroxide and zinc oxide were used for carbonation and dissolution.

### Carbonation of Cellulose

Carbonation of cellulose was done by reacting cellulose powders with treatment reagents such as ZnCl<sub>2</sub> (20-40 wt%), acetone or ethyl acetate, in a low temperature-high pressure reactor (Figure 1) at  $-5-0^{\circ}\text{C}$  and 30-40 bar of CO<sub>2</sub> for 2 hr. After carbonation, the cellulose carbonate was pressed and shattered before dissolving it. For ZnCl<sub>2</sub> system, washing (1-2 times) step was added before pressing process.

### Dissolution of Cellulose Carbonate

The pressed cellulose carbonate was dissolved in a sodium hydroxide solution at  $-5-0^{\circ}\text{C}$  and atmospheric pressure for 1

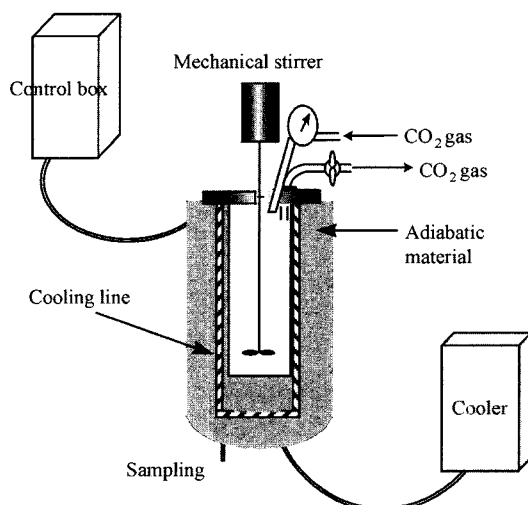
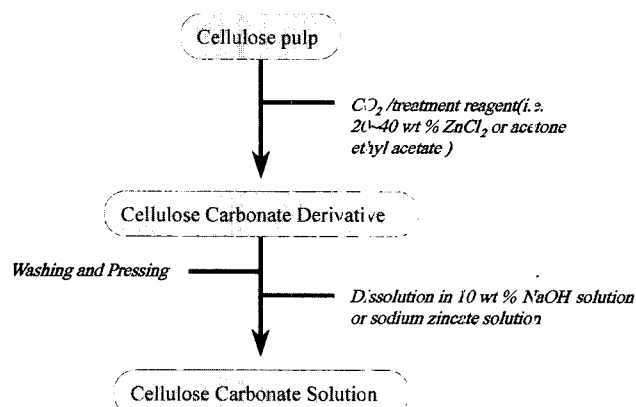


Figure 1. Reactor for carbonation of cellulose.



Scheme 2. Carbonation and dissolution of cellulose.

hr. In dissolution process, cooling system was used for controlling the dissolution temperature within  $\pm 0.2^{\circ}\text{C}$ . Zinc oxide was added within 100:0-100:3 wt ratio of 10 wt% NaOH:ZnO for dissolving cellulose carbonate. The cellulose carbonate solution was stored at  $5\pm 1^{\circ}\text{C}$  for analysis. The process of carbonation and dissolution of cellulose is shown in Scheme 2.

### Determination of Molecular Weight

Intrinsic viscosities of cellulose and cellulose carbonate were measured with an Ubbelohde viscometer using 0.5 M cupriethylenediamine hydroxide as a solvent at  $20^{\circ}\text{C}$  according to ASTM D1795 method. From the intrinsic viscosity, molecular weight was determined by the following equation (1)[10].

$$DP_w = [\eta] \times 190, M_w = DP_w \times 162 \quad (1)$$

where  $DP_w$  and  $M_w$  are the weight average DP and the weight average molecular weight of cellulose, respectively.

### Solubility of Cellulose Carbonate

The solubility of cellulose carbonate was evaluated by observing cellulose carbonate solutions with optical microscope (OPHOPHOT-POL, Nikon, Japan) at the magnification of 200. Absorbance indicating the turbidity of cellulose carbonate solutions was measured with a UV-Vis spectrophotometer (Shimadzu UV-2101PC, Japan).

### Phase Diagram of Cellulose Carbonate

Phase diagram of cellulose carbonate was obtained with the change of cellulose carbonate concentration and dissolution temperature. The solubility of cellulose carbonate in 10 wt% NaOH solution containing zinc oxide (0-3 wt%) was evaluated with stirring for 30 min. The temperature was controlled by decreasing from 15 to  $-12^{\circ}\text{C}$ .

### Viscosity Measurement of Cellulose Carbonate Solution

In order to evaluate stability of the cellulose carbonate

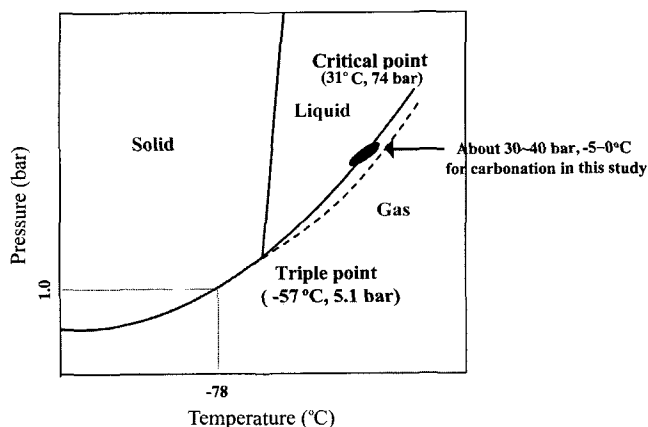
solution, its viscosity was measured with a Brookfield (RV DV-II<sup>+</sup>, spindle #06) viscometer at  $23 \pm 1^\circ\text{C}$ .

## Results and Discussion

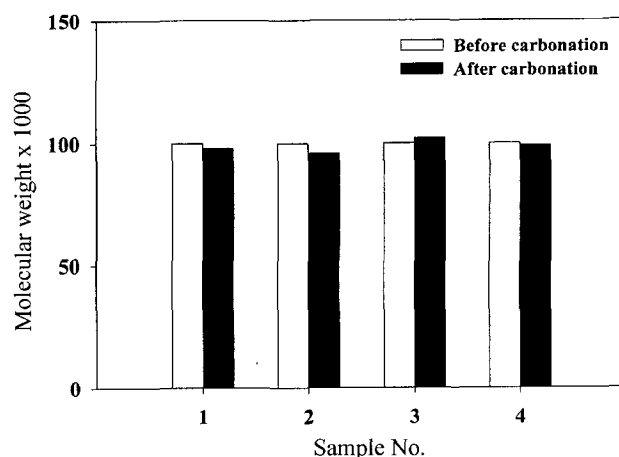
### Carbonation of Cellulose

The cellulose carbonate was prepared by reacting cellulose powder and  $\text{CO}_2$  gas with various treatment reagents for 2 hr. Based on the liquid phase condition of  $\text{CO}_2$  shown in Figure 2, carbonation conditions chosen in this study were  $-5$ – $0^\circ\text{C}$  and 30–40 bar of  $\text{CO}_2$  gas. Treatment reagents such as  $\text{ZnCl}_2$  systems, acetone and ethyl acetate were used for the purpose of enhancing the reaction of  $\text{CO}_2$  and cellulose because they increase the cellulose reactivity and  $\text{CO}_2$  solubility in carbonation medium. Additionally, the use of treatment reagent is expected to broaden the liquid phase region of  $\text{CO}_2$  and so the temperature and pressure for carbonation will be milder than the conditions used in this study.

The molecular weights of cellulose and cellulose carbonate were measured for investigating any change of molecular weight during carbonation. Their molecular weights were rarely changed as shown in Figure 3. The



**Figure 2.** Phase diagram of carbon dioxide (solid line; phase boundary of  $\text{CO}_2$  only, dashed line; shifted phase boundary of  $\text{CO}_2$  in treatment reagent).



**Figure 3.** Molecular weight change of cellulose by carbonation (treatment reagent of sample No. 1; 20%  $\text{ZnCl}_2$ , sample No. 2; 30%  $\text{ZnCl}_2$ , sample No. 3; acetone, and sample No. 4; ethyl acetate).

solubility of prepared cellulose carbonate stored in a refrigerator ( $-5$ – $0^\circ\text{C}$  and atmospheric pressure) was not changed for more than several months.

### Solubility of Cellulose Carbonate

Cellulose carbonates obtained with various treatment reagents were dissolved in 10%  $\text{NaOH}:\text{ZnO}$  (100:3 wt ratio) to prepare 3% cellulose carbonate solution. Solubility data of the cellulose carbonates are shown in Table 1. Ethyl acetate showed better solubility compared with other treatments reagents. The solubility of cellulose in sodium hydroxide solution could be significantly enhanced by adding zinc oxide or urea to the system and/or by lowering the temperature of the treatment [11,12]. Presence of zinc oxide led to an in-situ formation of zincate complex facilitating dissolution of cellulose chains such as short-chain part up to the DP of about 200, even at room temperature [13].

Table 2 shows the solubility of cellulose carbonate at various solvent compositions and cellulose carbonate concentrations. Gelation was observed at above 5 wt% of cellulose carbonate concentration. Generally, cellulose chains

**Table 1.** Solubility of 3% cellulose carbonate with the change of treatment reagent

Treatment reagent for carbonation	Solvent (wt ratio)				
	10% $\text{NaOH}:\text{ZnO}$ (100:3)	10% $\text{NaOH}:\text{ZnO}$ (100:2)	10% $\text{NaOH}:\text{ZnO}$ (100:1)	10% $\text{NaOH}:\text{ZnO}$ (100:0.5)	10% $\text{NaOH}$
40 wt% $\text{ZnCl}_2$	⊙	○	△	×	×
30 wt% $\text{ZnCl}_2$	⊙	○	△	×	×
20 wt% $\text{ZnCl}_2$	⊙	○	△	×	×
Acetone	⊙	○	△	×	×
Ethyl acetate	⊙	○	△	△	×

⊙; soluble, ○, △; soluble incompletely, ×; insoluble.

**Table 2.** Solubility of cellulose carbonate with the change of solvent composition and cellulose carbonate concentration

Solvent (wt ratio)	Cellulose carbonate concentration (wt%)	
	3-5	5.5
10% NaOH:ZnO(100:3)	⊙	⊙
10% NaOH:ZnO(100:2)	○	○
10% NaOH:ZnO(100:1)	△	Gelation
10% NaOH	△-Gelation	Gelation
10% NaOH:Urea(100:3)	○-△	Gelation
10% NaOH:ZnO:Urea(100:1:3)	⊙-○	○
10% NaOH:ZnO:Urea(100:2:3)	⊙	⊙

⊙; Soluble, ○, △; Soluble incompletely, ×; Insoluble.

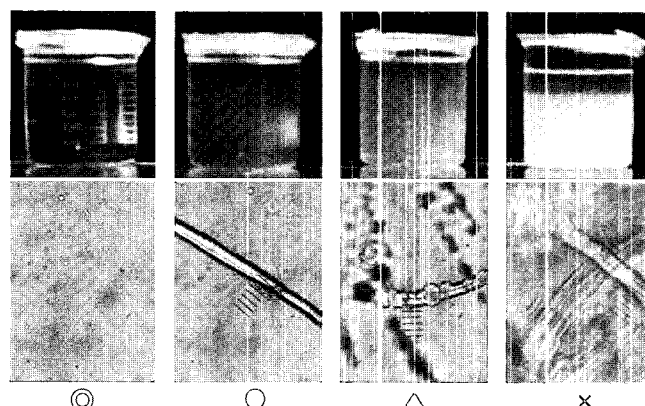
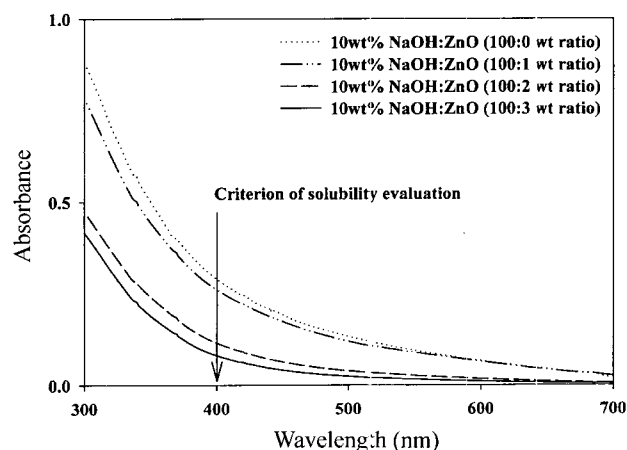
**Table 3.** Solubility of 5.5% cellulose carbonate with the change of dissolution- pressure

Solvent (wt ratio)	Dissolution pressure	
	Atmospheric pressure	30 bar (N <sub>2</sub> )
10% NaOH:ZnO(100:3)	⊙	⊙
10% NaOH:ZnO(100:2)	○	○
10% NaOH:ZnO(100:1)	Gelation	Gelation
10% NaOH	Gelation	Gelation
10% NaOH:Urea(100:3)	Gelation	Gelation
10% NaOH:ZnO:Urea(100:1:3)	Gelation	Gelation
10% NaOH:ZnO:Urea(100:2:3)	⊙	⊙

⊙; Soluble, ○, △; Soluble incompletely, ×; Insoluble.

interact with each other through hydrogen bonding and van der Waals forces to form extensive crystalline regions. Since these inter-chain hydrogen bonds in the crystalline regions present a formidable barrier to penetration of reagents, cellulose is insoluble in most of liquids including water and polar organics. At certain cellulose carbonate concentration, gelation occurred due to the aggregation of cellulose derivatives. These aggregates consist of highly ordered cylindrical core of aligned chains with two spherical coronas surrounding core ends which have an effect on cellulose solubility[14]. Table 3 shows the solubility of cellulose carbonate depending on dissolution pressure. 5.5% cellulose carbonate solution was prepared at different zinc oxide content in a sodium hydroxide solution. From the results shown in Tables 2-3, the zinc oxide concentration for dissolving cellulose carbonate up to 5.5 wt% was 100:3 wt ratio of 10% NaOH:ZnO.

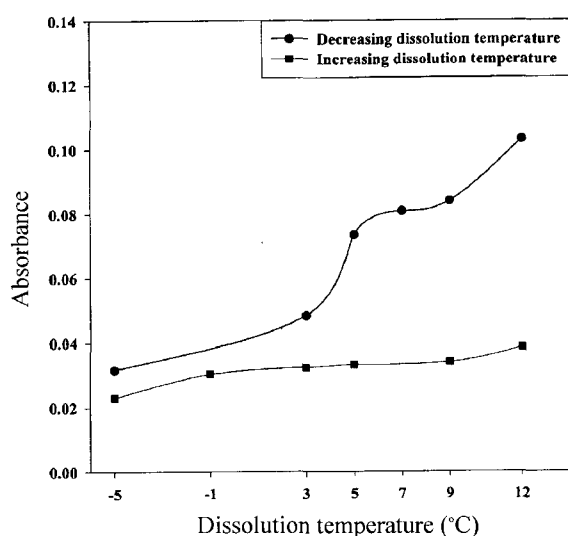
The optical microphotographs of cellulose carbonate solutions with different solubility (Tables 2-3) are shown in Figure 4. In soluble cases of cellulose carbonate (⊙), solutions were transparent with no microfibrer. In incompletely

**Figure 4.** Optical microphotographs of cellulose carbonate solutions ( $\times 200$ , Line gage;  $10 \mu\text{m}$ ), (⊙; Good soluble, ○; Medium soluble, △; Poor soluble, ×; Insoluble).**Figure 5.** UV-Vis spectra of 3% cellulose carbonate solution at different solvent composition.

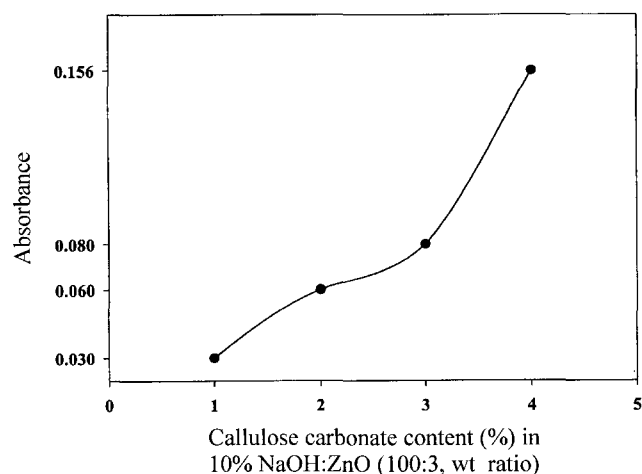
soluble cases (○, △), solutions became opaque and some swollen microfibrer with a diameter of ca.  $20 \mu\text{m}$  were observed. In insoluble cases (×), they showed highly swollen fibrous phase. The difference in solubility of cellulose carbonate was attributed to the solvent power and degree of substitution. Even though substitution of cellulose proceeded with the same reagent, the solubility would be different depending on substitution position. For example, carboxymethyl cellulose substituted at C-2, C-3, and C-6 hydroxyl group simultaneously would be dissolved in water. On the other hand, carboxymethyl cellulose substituted at the C-6 hydroxyl group only was insoluble in water[14].

UV-Vis spectra of 3% cellulose carbonate solutions at various solvent compositions are shown in Figure 5. Dissolution conditions were  $-5-0^\circ\text{C}$ , 30 min of stirring and atmospheric pressure. The cellulose carbonate solutions were kept at  $5^\circ\text{C}$  for 24 hr under atmospheric pressure and

then analyzed by UV-Vis spectrophotometer. The absorbance was increased with decreasing zinc oxide content in 10% sodium hydroxide solution. This is consistent with the results of Figure 4. Since the difference of absorbance between solutions was clearly distinguished at 400 nm in visible light spectrum, absorbance at 400 nm was used for criterion of solubility evaluation. Figure 6 shows the UV absorbances of 1% cellulose carbonate solution at 400 nm with decreasing and increasing the dissolution temperature. The cellulose carbonate solution with increasing temperature showed very slight increase of absorbance but that with



**Figure 6.** UV-Vis absorbances at 400 nm of 1% cellulose carbonate solution in 10% NaOH:ZnO (100:3 wt ratio) with decreasing and increasing the dissolution temperature.



**Figure 7.** UV-Vis absorbance at 400 nm of cellulose carbonate solutions with various cellulose carbonate concentration in 10% NaOH:ZnO (100:3 wt ratio) (dissolution temperature  $-1^{\circ}\text{C}$ ).

decreasing temperature showed abrupt increase of absorbance in the range of 3-12°C. The cellulose carbonate solution prepared at lower temperature was somewhat more stable than that prepared at higher temperature. So the experimental procedure of decreasing the temperature was used to get the phase diagram of cellulose carbonate.

Figure 7 shows the UV absorbance of cellulose carbonate solutions at various concentration. The absorbance was increased abruptly with increasing cellulose carbonate concentration. From this result, the concentration dependence of UV absorbance was taken into consideration for plotting the phase diagram.

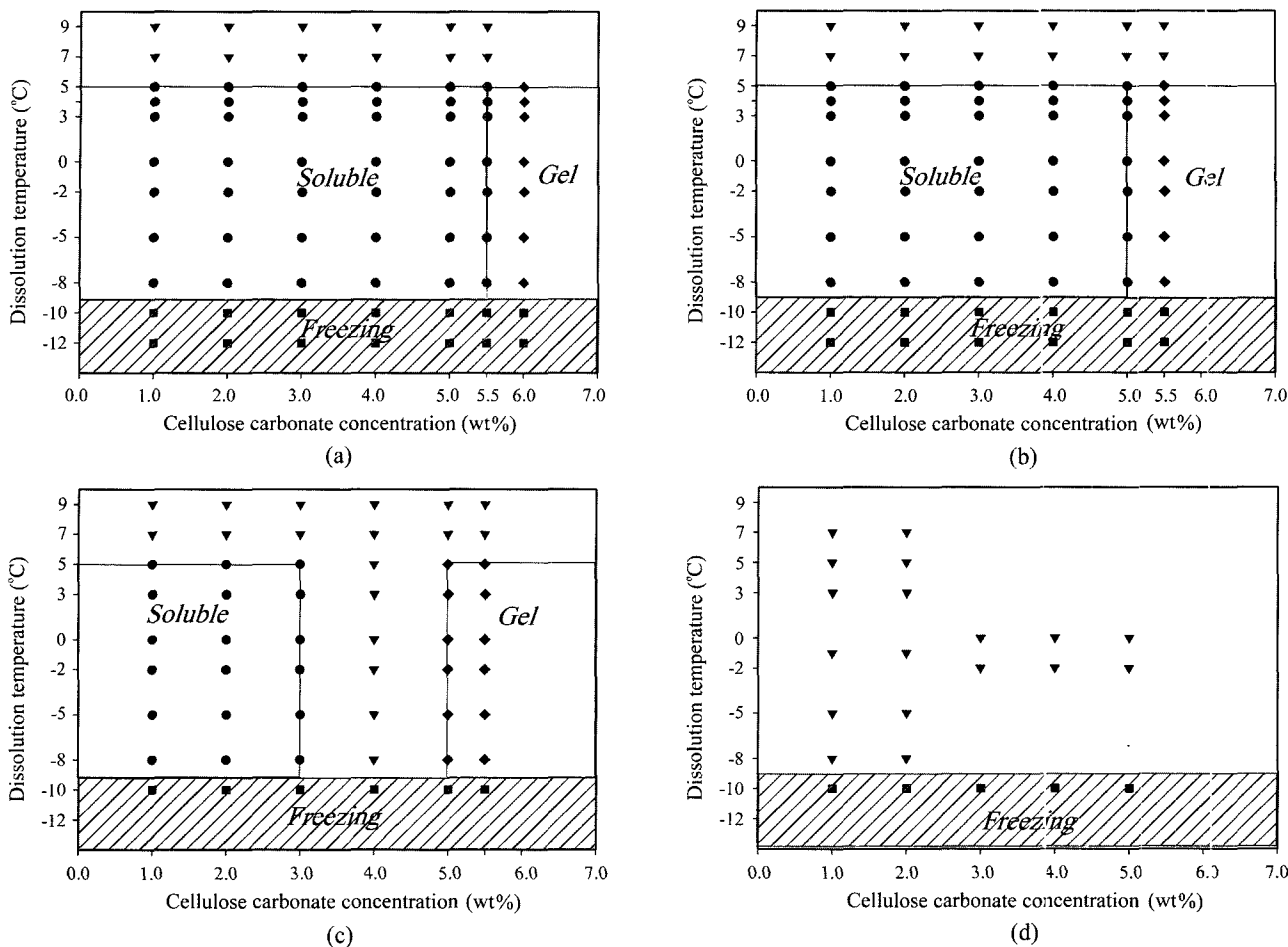
### Phase Diagram of Cellulose Carbonate

Figure 8 shows the phase diagram of cellulose carbonate consisting of cellulose carbonate concentration and dissolution temperature at various solvent compositions. Regardless of cellulose carbonate concentration and zinc oxide content, the zone of dissolution (●) appeared at  $-8$ - $5^{\circ}\text{C}$  and those of poor or insoluble (▼) and that of freezing (■) appeared at above  $5^{\circ}\text{C}$  and below  $-8^{\circ}\text{C}$ , respectively. Boundary of soluble (good to medium soluble, ●), insoluble (poor to insoluble, ▼) and gelation (◆) zones was dependent on cellulose carbonate concentration and zinc oxide content at  $-8$ - $5^{\circ}\text{C}$ . The cellulose carbonate concentration for starting gelation was increased with increasing zinc oxide content in a sodium hydroxide solution. When zinc oxide content increased up to 3 wt%, the gelation appeared at higher than 5.5 wt% of cellulose carbonate concentration. Maximum concentration of cellulose carbonate for soluble zone was increased with increasing zinc oxide content. These results indicate that the factors affecting cellulose carbonate solubility are temperature, cellulose carbonate concentration and zinc oxide content in a sodium hydroxide solution.

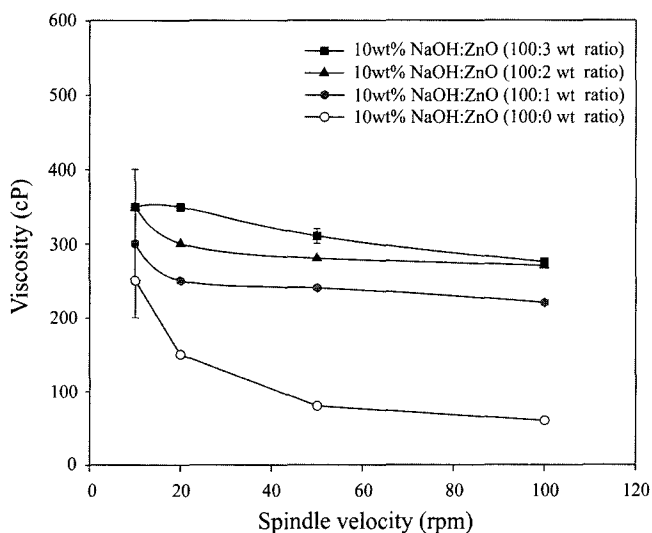
### Viscosity Measurement of Cellulose Carbonate Solution

The viscosity was measured at different solvent compositions and spindle velocities as shown in Figure 9. The viscosity was increased with increasing zinc oxide concentration in a sodium hydroxide solution and the highest viscosity was obtained at 100:3 weight ratio of 10 wt% NaOH:ZnO. As already shown in Figures 4-8, better dissolution state was obtained at higher content of zinc oxide in a sodium hydroxide solution.

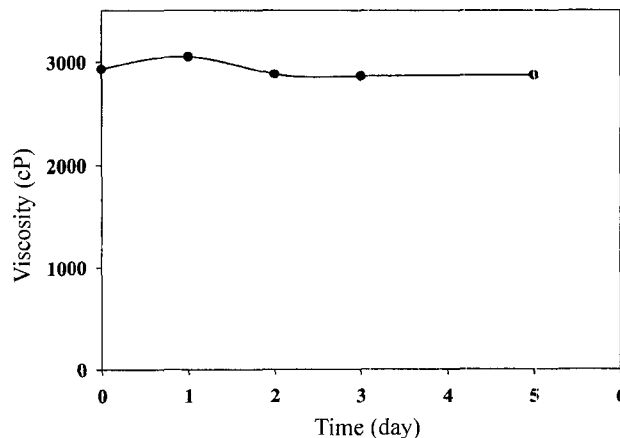
Cellulose carbonate was dissolved at low temperatures ( $-5$ - $0^{\circ}\text{C}$ ) because it is exothermic when cellulose is dissolved in a sodium hydroxide solution [15,16]. Yamashiki *et al.* [17] obtained good cellulose solutions within 9-10% sodium hydroxide at a temperature of about  $-10^{\circ}\text{C}$  and DP of about 200 with a cellulose concentration up to 5%. At lower temperature, the cellulose carbonate was better soluble and had higher viscosity. In order to investigate the stability of cellulose carbonate solution, viscosity was measured with increasing storage time. Viscosity was not changed up to 5



**Figure 8.** Phase diagrams of cellulose carbonate at different concentration and solvent composition of 10% NaOH:ZnO (wt ratio); (a) 100:3, (b) 100:2, (c) 100:1, (d) 100:0 (●: good to medium soluble, ▼: poor to insoluble, ■: freezing, ◆: gelation).



**Figure 9.** Viscosities of cellulose solutions with the change of solvent composition and spindle velocity.



**Figure 10.** Viscosity change of cellulose carbonate solution with time.

days at refrigerator ( $-5-0^{\circ}\text{C}$  and atmospheric pressure), as shown in Figure 10. This indicates the feasibility of cellulose

carbonate for practical use.

### Conclusions

Cellulose carbonate obtained by reacting carbon dioxide onto cellulose pulp (DP 850) was dissolved in a sodium hydroxide solution. Combining the solubility evaluation by optical microscopic observation, UV absorbance and viscosity measurements, phase diagram of cellulose carbonate was obtained. Results were summarized as follows.

1. Cellulose carbonate was obtained by reacting cellulose with carbon dioxide and treatment reagents, i.e.,  $ZnCl_2$ , acetone or ethyl acetate. Among them, ethyl acetate was the most effective.

2. The molecular weight of cellulose was rarely changed by carbonation. Cellulose carbonate and its solution was stable in refrigerator ( $-5-0^\circ C$  and atmospheric pressure).

3. The addition of zinc oxide in sodium hydroxide solution significantly enhanced the solubility of cellulose carbonate. Cellulose carbonate solution in good soluble zone was transparent and showed the lowest in absorbance and the highest in viscosity.

### Acknowledgement

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