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Reactivity of Ethylene Carbonate and Glycols as Solvolysis Reagents of Lignocellulose

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The solvolysis reaction of lignocellulose using ethylene carbonate (EC) and/or glycols as solvolysis reagents was studied. Reaction of EC in the solvolysis of lignocellulose was examined by NMR and GPC. NMR data showed that EC changed into polyethylene glycol types of polymers with the release of carbon dioxide, and no polycarbonate type of unit was observed in the reactant. Remaining content of EC was estimated by the loss of weight after the reaction caused by the production of carbon dioxide due to the decomposition of EC. The EC remaining content decreased with solvolysis time. Using higher acid condition and higher temperature accelerated the decomposition of EC. GPC data showed that the molecular weight of the reactant increased with solvolysis time. The increase of molecular weight of solvolyzed product might be due to the polymerization of degraded lignocellulose as well as the polymerization of EC.
Key words: cellulose, ethylene carbonate, lignocellulose, solvolysis, wood

1. INTRODUCTION

Solvolysis of lignocellulose has been studied as a pulping technique for producing pulp and paper. In this pulping technique (solvolysis pulping), lignocellulose such as wood chips was treated with organic solvents such as alcohols [1] and phenols [2] as reaction media to remove lignin from wood without degrading cellulose fiber. Producing high-quality cellulose is a key point of solvolysis pulping, therefore it is important to control the reaction condition so as not to degrade cellulose.

Since the early 1990s, the solvolysis technique has been applied to a chemical conversion of wood to produce bio-based polymer resources. Kurimoto *et al.* applied polyethylene glycol (PEG) and glycerin (Gly) for degrading wood to obtain liquid products in the presence of sulfuric acid catalyst [3]. Ono *et al.* used phenols and acid catalyst to obtain solvolyzed wood and produced phenol resin types of wood adhesives [4]. In these techniques, much more severe reaction conditions were used compared with those for solvolysis pulping, to promote the degradation of cellulose.

Recently, solvolysis of lignocellulose has been greatly improved for the production of useful chemicals from biomass. Cyclic carbonates such as ethylene carbonate (EC) were used as an effective accelerator of the solvolysis reaction of lignocellulose [5]. When EC was used as a reaction medium, it led a severe reaction condition for acid catalyzed solvolysis of lignocellulose, and cellulose was rapidly converted into the levulinic acid structure (Solvolysis System) [6]. Levulinic acid is well known as a useful platform chemical that can be used for many useful materials such as fuel additives, herbicides and polymer resources [7]. Conventional levulinic acid production has been carried out using acid catalyzed thermo hydrolysis of lignocellulose. However, the hydrolysis produces highly condensed acid lignin that has low reactivity and is not suitable for material applications. On the other hand, levulinic acid production in the solvolysis system generated a useful lignin fraction that had higher reactivity and could be used as polymer resources [8].

In this paper, the behavior of EC in the solvolysis reaction of lignocellulose is studied. The data will provide basic information for the solvolysis technique, especially for recovering of solvolysis reagents.

2. EXPERIMENT

2.1 Materials

Japanese cedar wood meal (30-80 mesh) and commercial cellulose powder (α-cellulose, SIGMA Chemical Co.) were used as lignocellulose samples. They were dried in an oven at 105°C for 12 hr and kept in a desiccator at room temperature before being used. All the other chemicals used were extra pure grade reagents in accordance with the Japanese Industrial Standard (JIS) and used as received.

2.2 Solvolysis treatment

The flask contained a mixture of 5 g of a solvolysis reagent such as EC, ethylene glycol (EG), diethylene glycol (DEG), glycerin (Gly), and polyethylene glycol (PEG). Then, 0.05 to 0.25 g (1 to 5 wt% for the solvolysis reagent) of 97% sulfuric acid was added into the flask. 1 g of lignocellulose was then added to the flask and mixed well. The flask was immersed in an oil bath preheated at 120°C to 150°C to start the solvolysis reaction. Every solvolysis reaction was carried out under atmospheric pressure. After a preset time, the flask was immersed in cold water to quench the reaction. The resultant was diluted with 300 ml of 80% 1,4-dioxane. The dioxane diluted resultant was separated into residue and filtrate with an ADVANTEC

GA100 glass filter. The filtrate was neutralized with 1 M of sodium hydroxide solution. The solvolyzed product was obtained by the removal of dioxane and water from the dioxane soluble part with a rotary evaporator under reduced pressure at 30-40°C.

2.3 Analysis of the solvololyzed product

GPC analysis of the solvolyzed product was performed with a Shimadzu LC-6A (Shimadzu Co.) equipped with two columns of Shodex KD-806M and KD-802 in series. N,N-dimethylformamide mixed with 0.01M of LiBr was used as the eluent. Chromatogram was monitored with a refractometer. The molecular weight of the product was calculated based on the standard polyethylene oxide.

^{1}H NMR analysis of the solvolyzed product was performed with a JEOL Lambda 400 MHz spectrometer using DMSO-d_6 as a solvent.

3. RESULTS AND DISCUSSION

3.1 Chemical structure of the reacted EC

Reaction of EC in the solvolysis was monitored by ^{1}H-NMR spectrometer (Fig. 1). The signal of 4.5 ppm shows the methylene proton of EC. This signal decreased with the solvolysis time, and almost disappeared at 60 min. On the other hand, the signal of the methylene proton of polyethylene oxide unit (3.5 ppm) increased with the solvolysis time and became the main signal of the spectrum at 60 min of solvolysis. The signal at 3.4 ppm shows the methylene proton of the hydroxyl group part of the polyethylene oxide unit. This signal appeared clearly at the initial stage of the reaction then decreased with solvolysis time. This ^{1}H-NMR data suggested that ethylene carbonate decomposed into a polyethylene oxide type of polymer with solvolysis time.

Vogdanis and Heitz [9] studied the polymerization reaction of EC and reported that the chemical structure of the polymer was a polyethylene glycol type of polymer (Fig. 3-(2)) and polycarbonate type of polymer (Fig. 3-(3)). EC could produce a carbonate type of polymer in the solvolysis of lignocellulose. If a carbonate type of polymer existed in the reactant, the methylene proton of the carbonate unit would appear at 4.3 ppm [10]. Fig. 1 shows no signal at this region, suggesting that there were no poly carbonate types of polymers in the solvolyzed product. It has been reported that EC decomposed into ethylene glycol with the release of carbon dioxide in water solution in the presence of acid [11] (Fig. 3-(1)). However, it might be a minor reaction due to the small amount of water in the solvolysis reaction media. It is concluded that in the chemical reaction of EC, EC is mainly converted into a polyethylene glycol type of polymer in the solvolysis reaction of lignocellulose.

Fig. 2 shows ^{1}H-NMR of the model reaction of solvolysis using EC with sulfuric acid. The NMR spectra led to exactly the same results as those shown in Fig. 1. Although the spectra shown in Fig. 1 were the solvolyzed product of cellulose, the large signals were mainly from EC and its derivatives. This might have been due to the large amount of EC in the reaction condition of cellulose/EC (1/5, w/w).

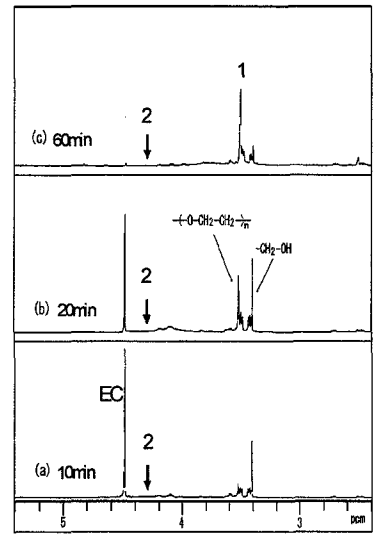

Fig.1 ^{1}H-NMR spectra of solvolysis products of cellulose at 10 min (a), 20 min (b), and 60 min (c) of the reaction time.

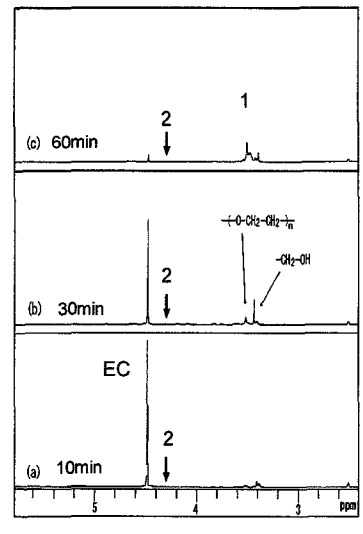

Fig. 2. ^{1}H-NMR spectra of the model solvolysis using EC with 5 wt% of sulfuric acid at 10 min (a), 30 min (b), and 60 min (c) of the reaction time.

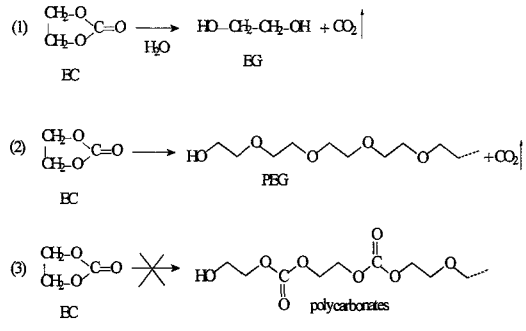

Fig. 3. Decomposition and ring opening polymerization of EC in the solvolysis

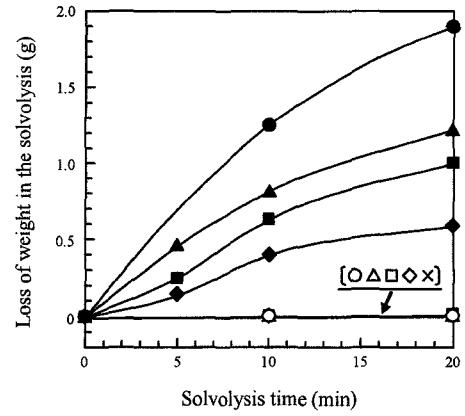

Fig. 4. The loss of weight in the solvolysis reaction of cellulose at 140 °C at the solvolysis systems of using, EG○, DEG △, PEG200 □, PEG400 ◇, and PEG600× at 3 wt % of sulfuric acid, and EC in the sulfuric acid condition of 1 wt% ◆, 2 wt%■, 3 wt%▲, and 5 wt%●.

3.2 Remaining content of EC

As shown in Fig. 3, when EC is converting into a polyethylene oxide type polymer, it releases carbon dioxide. Therefore, the remaining content of EC can be estimated by measuring the loss of weight after the reaction caused by the production of carbon dioxide due to the decomposition of EC. Fig. 4 shows the loss of weight in the solvolysis reaction of cellulose for the solvolysis systems of EC, EG, DEG, PEG200, PEG400, and PEG600 (numbers after PEG are the average molecular weight) at 140°C. No weight losses were observed in the systems using glycols such as EG, DEG, and PEGs. On the other hand, a considerable weight loss was observed when EC was used as the solvolysis reagent. This suggests that the loss of weight is mainly caused by the reaction of EC. As shown in Fig. 4, the reaction of EC using higher acid condition resulted in a higher loss of weight.

Table I shows the remaining percent of EC in the cellulose solvolysis systems using EC at 140°C and 150°C in the presence of 1 to 5% of sulfuric acid. The data were calculated by the following procedure. In the solvolysis system of EC using 5 wt% of sulfuric acid at 140°C, the loss of weight reached 1.9 g at 20 min of reaction (Fig. 4). When one mole of EC degrades into a glycol type of compound, it releases one mole of carbon dioxide. When all EC in the system (5 g) has decomposed, the weight loss will be 2.5 g theoretically. Therefore, the remaining percent of EC was calculated by [(2.5-1.9)/2.5]×100 = 24%. As shown in Table I, the amount of remained EC decreased with reaction time. Higher sulfuric acid concentration and higher reaction temperature accelerated the decomposition of EC.

Table II shows the remaining percent of EC in several solvolysis systems of wood. The solvolysis system of EC/EG (8/2, w/w) is a practical solvolysis system to achieve the efficient solvolysis reaction of wood [5]. The data were calculated by the same equation shown above. The remaining percent of EC varied depending on the reaction condition. Under severe reaction conditions, such as high acid condition, the remaining rate of EC decreased.

Table I. Remaining percent of EC in the solvolysis of cellulose

	140 °C[1]			
Time (min)	1 wt%[2]	2 wt%[2]	3 wt%[2]	5 wt%[2]
0	100.0	100.0	100.0	100.0
5	94.4	90.0	81.6	100.0
10	84.0	74.8	67.6	50.0
20	76.4	60.0	51.2	24.0
	150 °C[1]			
Time (min)	1 wt%[2]	2 wt%[2]	3 wt%[2]	5 wt%[2]
0	100.0	100.0	100.0	100.0
5	87.6	81.6	71.2	52.4
10	83.2	70.8	62.0	41.6
20	71.2	50.4	30.8	11.2

[1] Solvolysis reaction temperature.
[2] Weight percent of sulfuric acid to the solvolysis reagent

Table II. Remaining percent of EC in the solvolysis of wood

	EC[1]		EC/EG (8/2, w/w)[1]	
Time (min)	3 wt%[2]	5 wt%[2]	3 wt%[2]	5 wt%[2]
0	100.0	100.0	100.0	100.0
10	79.2	66.4	77.5	65.0
20	60.0	46.0	56.5	38.5
40	38.0	2.8	17.5	NA[3]

[1] Solvolysis reagent.
[2] Weight percent of sulfuric acid to the solvolysis reagent
[3] Not analyzed

3.3 Molecular weight of the solvolysis product

Fig. 5 shows the GPC profile of the model reaction using EC. The model reaction of the solvolysis was carried out using EC and 5 wt% of sulfuric acid without any lignocellulose. The data showed that the molecular weight of the product increased with solvolysis time, indicating that EC itself was converted into polymer in the solvolysis condition.

Fig. 6 shows the GPC profile of the solvolyzed product of cellulose using EC. The chromatograms showed that the broad peak appearing in the high molecular weight region shifted, and the average molecular weight of the products increased with reaction time. This would be caused by the polymerization of decomposed products of cellulose as reported before [12], as well as the polymerization of EC.

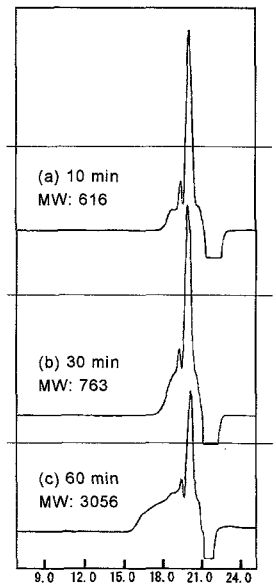

Fig. 5. GPC profiles of the reactant at the solvolysis model reaction at 150 °C using EC and 5wt% of sulfuric acid, at the reaction time of 10 min (a), 30 min (b), and 60 min (c).
MW: weight average molecular weight.

4. CONCLUSION

The reaction of EC decomposition in the solvolysis reaction of lignocellulose was studied. NMR analysis of the solvolysis products showed that the chemical structure of the decomposed EC mainly consisted of the polyethylene glycol type of polymer. Since EC released carbon dioxide as it decomposed, the remaining content of EC was calculated by measuring the loss of weight in the solvolysis reaction. The remaining content of EC decreased with solvolysis time. Severe reaction conditions such as under high temperature and high acid concentration accelerated the decomposition of EC. The polymerization of EC was one of the reasons for the increase of molecular weight of the solvolyzed product.

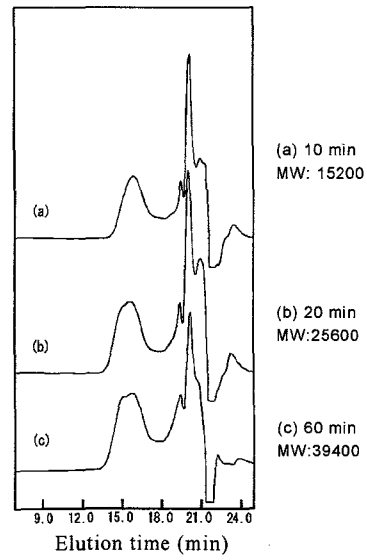

Fig. 6. GPC profiles of the product of the cellulose solvolysis at 150 °C using EC and 5wt% of sulfuric acid, at the reaction time of 10 min (a), 20 min (b), and 60 min (c).
MW: weight average molecular weight.

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