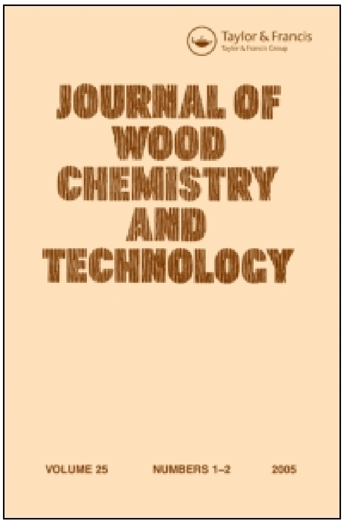

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NOVEL WOOD PROCESSING BY MALEIC ACID - GLYCEROL MIXTURE SYSTEM: IMPROVEMENT OF WATER RESISTANCE AND MECHANICAL PROPERTY OF CELLULOSE BY THE PROCESSING

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ABSTRACT

Maleic acid (M) - glycerol (G) mixture (MG) treatment for woods have been developed for improvement of water resistance and durability of woods and particle boards. Characteristics of MG and the mechanical strength of MG-treated cellulose as a model of wood were investigated to clarify the effect of MG treatment. Formation of ester bond between M and G was found during the preparation of MG solution, resulting in production of polyesters with more than 1,000 of molecular weight. Double bonds in M were maintained after the reaction of MG with cellulose. Reaction temperature of MG with cellulose over 180 ℃ affected a decrease in the moisture content and the reinforcement of tensile strength of filter paper.

INTRODUCTION

Wood and wood composite materials, especially particle board were inferior to metal and plastics with respect to water resistance. Thus acylation of wood has been studied to improve water resistance due to the protection of hydroxyl groups[1,2]. MG treatment for wood, one of the acylation, was developed in 1987 to improve not only the water resistance but also dimensional stability and mechanical strength[3,4]. Hypothesis of the functional mechanism was proposed as follows[3]: M reacted with G and simultaneously carboxylic groups of M reacted with the hydroxyl groups of cellulose component in wood by forming ester bonds, resulting in the cross-linkage of MG between the chains of cellulose to form a network structure. The network structure contributed to the dimensional stability in addition to suppressing hygroscopicity of hydroxyl groups. The formation of ester bonds between M and G has been perceived to occur at the step of the reaction with cellulose by heating.

The ester bonds between M and cellulose have been also revealed by the preliminary experiment[5]. However, whether bonding occurs between M and G or not and, if formed, when is the bonding produced have remained unknown. Moreover, direct evidence of covalent bonds between three components, cellulose-M-G, has not been clear yet.

In this study, the bonding manner between cellulose-M-G in addition to that between M-G was investigated to elucidate the cross-linkage of MG between the chains of cellulose. Furthermore, preparation conditions of MG-treated cellulose were examined to clarify the effective improvement of the water resistance and mechanical strength of cellulose.

RESULTS AND DISCUSSION

Formation of ester bond between maleic acid and glycerol

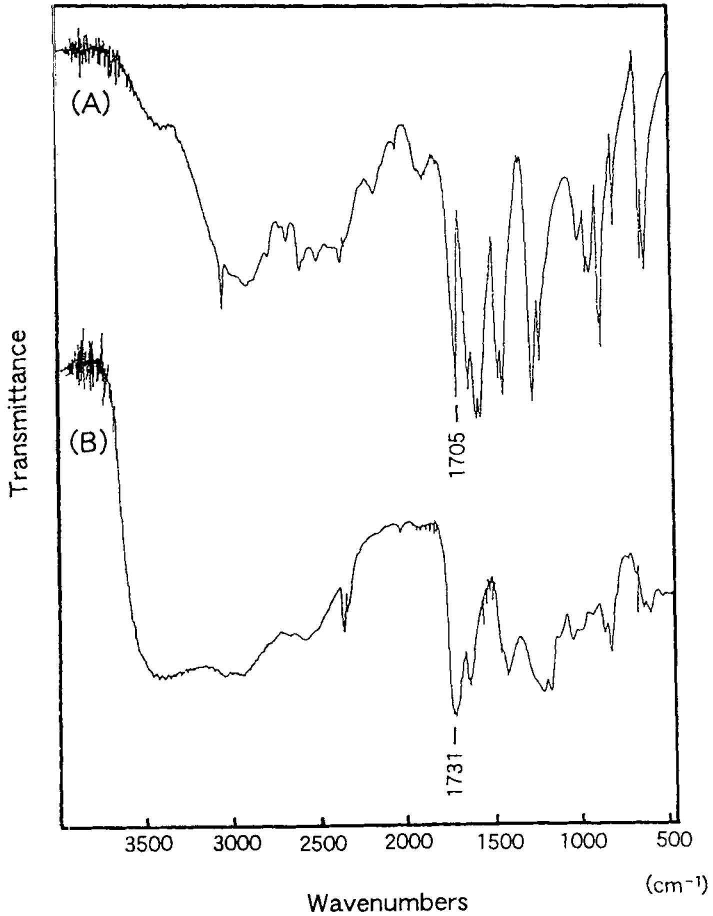


FIGURE 1. FT-IR Spectra of Maleic Acid (A) and MG (B).

dissolved in G under 100 °C. It had not been clarified whether the covalent bonding between M and G in the solution occurred or not. Characteristics of the MG solution were investigated at the beginning of this study.

The MG solution was coagulated to a solid at room temperature. IR spectra of M and MG solid were recorded using the KBr method (Fig. 1).

A peak of conjugated carbonyl groups in the spectrum of M was observed at 1705 cm^{-1}. However the peak in that of MG was shifted to 1731 cm^{-1} that was similar to the wavelength of carbonyl groups in diethyl maleate[6]. It might suggest that ester bonds between the carboxyl groups of M and the hydroxyl groups of G were formed on the preparation of MG solution.

^{1}H-NMR spectra of MG mixture in D_2O before and after heating was measured, as shown in Fig. 2. The spectrum of MG mixture before dissolution in Fig. 2(A) shows four signals ascribed to both the intact M and G; three signals at 3.51 - 3.81 ppm is assigned to G reffering to the spectrum of G alone in D_2O [δ 3.54 (dd, CH_2), δ 3.64 (dd, CH_2) and δ 3.77 (m, CH)] and singlet signal at 6.43 ppm is assigned to vinyl proton of M[7]. Several new signals at 3.97 - 4.50 and 6.49 - 6.58 ppm in Fig. 2 (B) appeared after the dissolution with heating (100 ℃). These signals seem to result from the down-field shift owing to the formation of an ester bond. Further new signals at 6.85 ppm and 6.90 ppm were observed, which were assigned to the vinyl proton of fumaric acid and/or fumarate ester[7]. An integral area ratio of signals of fumaric vinyl protons to that of maleic protons is about 4%. The double bond (*cis* form) of maleate in the polyester of anM and 1,6-hexanediol was isomerized to fumaric vinyl group (*trans* form) by heating at 187 ℃ during the preparation[8]. In this experiment, a little isomerization of the double bond was suggested to occur even below 100 ℃.

The formation of ester bonds was followed quantitatively by the acid value and saponification value. Complete dissolution of M in G took about 1-1.5 h. However, the values were examined until 3h and represented as mole percentage based on the amount of carboxyl groups of M. Fig. 3 showed that a decrease in the acid values was comparable to an increase in saponification values, suggesting that the carboxyl group of M and anM was consumed in the ester bonds. The formation of ester bond occurred rapidly durng complete dissolution by heating, and then continued gradually. Saponification value of anM was larger than M. Thus, AnM reacted with G even while mixing without heating.

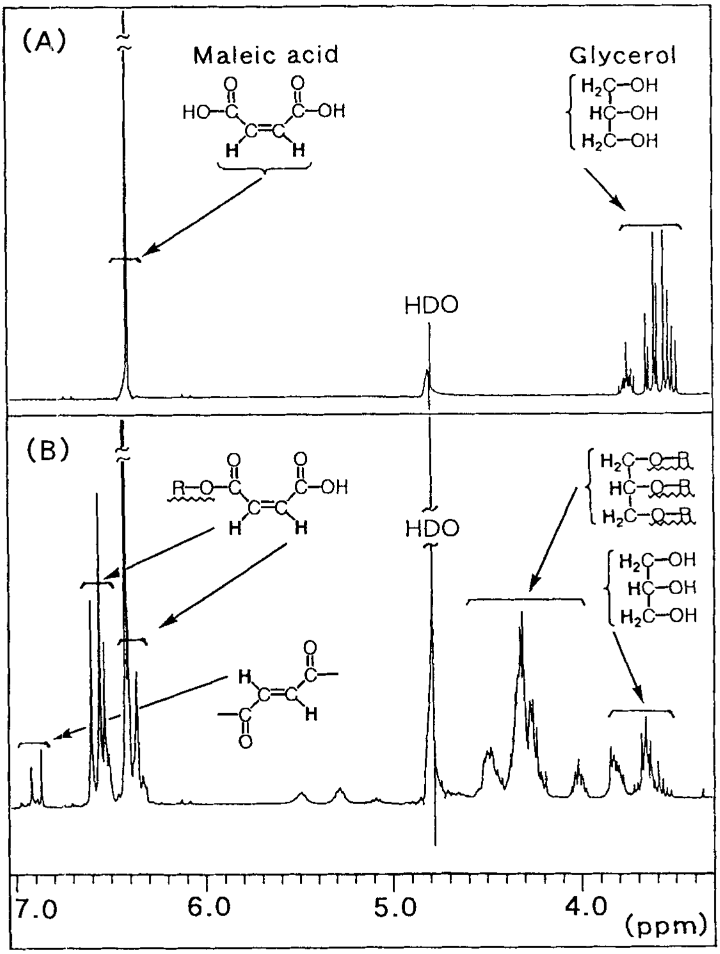


FIGURE 2. ^{1}H-NMR Spectra of MG before (A) and after (B) heating.

Molecular weight (MW) was measured to define the condensed structure of ester compounds. Field desorption-mass spectrum shows several large peaks, M/z 190, 288, 540 and 558. Proposed models corresponding to those M/z are shown in Fig. 4. Model 3 with M/z 540

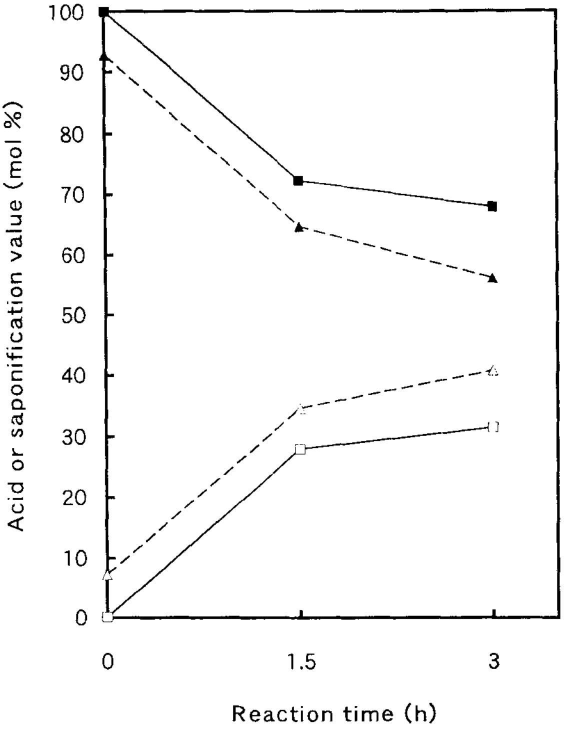
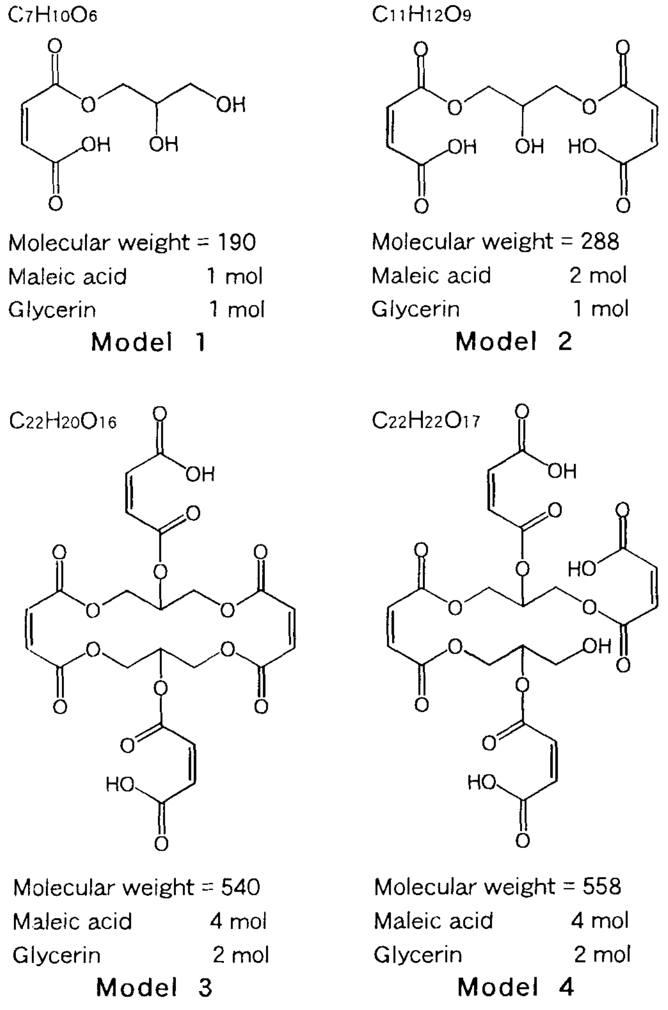


FIGURE 3. Acid and Saponification Values of MG and anMG.
—■— :Acid Value of MG, —□— :Saponification Value of MG
--▲-- :Acid Value of anMG, --△-- :Saponification Value of anMG

consisted of 4 mole of M and 2 mole of G representing that all hydroxyl groups of G are involved in ester bonds, and two carboxyl groups are free. Model 4 with M/z 558 consisted of 2 mole of G, all hydroxyl groups of one mole of G also involved in ester bonds, and two hydroxyl groups of the other G were consumed by the esterification. In addition a few of peaks were observed at more than M/z 1,000. These proposed models might suggest that a three dimensional network structure was formed by the condensation of MG as a terminal of G.



Molecular weight = 190
Maleic acid 1 mol
Glycerin 1 mol
Model 1

Molecular weight = 288
Maleic acid 2 mol
Glycerin 1 mol
Model 2

Molecular weight = 540
Maleic acid 4 mol
Glycerin 2 mol
Model 3

Molecular weight = 558
Maleic acid 4 mol
Glycerin 2 mol
Model 4

FIGURE 4. Proposed Models of MG Oligomers.

So large MW was estimated by gel filtration chromatography (GFC) with references of polyethylene glycols and ethylene glycol (Fig. 5). A few peaks in the chromatograph of anM dissolved in G for 1.5 h (anMG1.5; the others were abbreviated with the same manner)

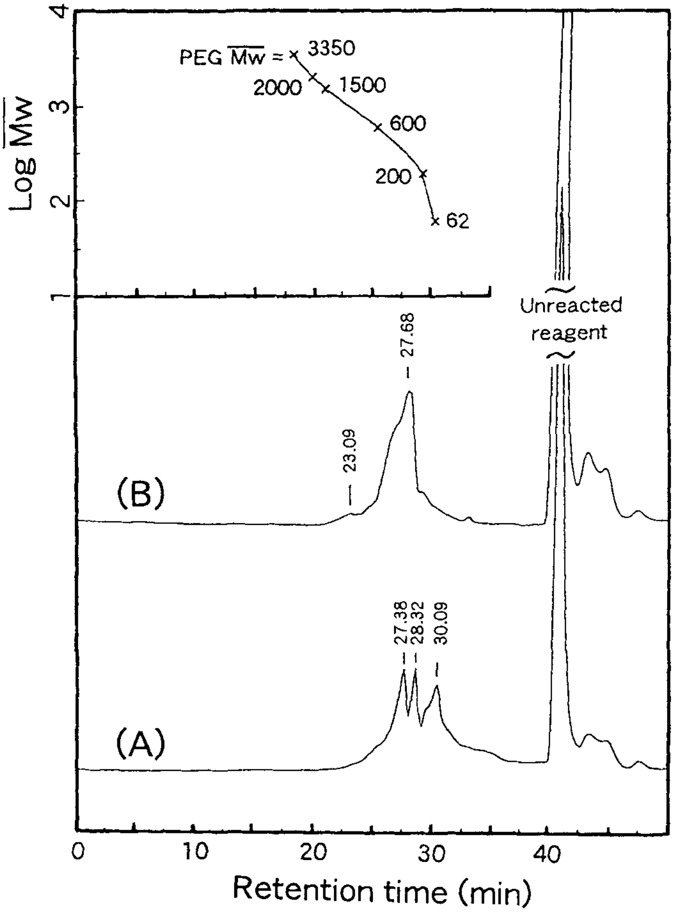


FIGURE 5. Gel Filtration Chromatograms of anMG1.5 (A) and anMG3.0 (B).

appeared and seemed to be shifted to lower retention time by prolongation of dissolution time (anMG3.0). That is to say that 390 of weight-average MW ($\overline{Mw}$) of anMG1.5 increased to 480 of anMG3.0. Furthermore the chromatograph of anMG 3.0 shows the peak at 23.1 min, indicating the formation of polyester with $\overline{Mw}$ greater than 1,200.

Similar tendency such as increase in $\overline{Mw}$ with prolongation of dissolution time was observed for MG. However, the Mw values of MG1.5 and MG3.0 ($\overline{Mw}$=210 and 350, respectively) were smaller than those of corresponding anMG. As normally predicted, these phenomena suggested that acid anhydride agent is more reactive than the corresponding acid. Therefore, anM is a very suitable agent for the esterification of woods with regard to both reactivity and economy, because anM is a cheaper chemical compared with M.

Though MW in this experiment was estimated from GFC, the intrinsic MW seems to be much larger than the experimental value. The reason resulted from that the peaks of unreacted agents for anM-G mixture after 40 min retarded remarkably compared with that of ethylene glycol at 30 min as a minimum standard of MW . This phenomena might be explained by two assumptions. One is that the used compounds, M and G, were interacting with the substrate of the column. The other is that the MG polyesters have packing structure, i.e. more dense network structure of MG by cyclization, as represented in model 3 of Fig. 3, than linear polymer. Thus, the MG polyesters formed have rather high MW.

MG bind to cellulose

A previous report has revealed that the weight of filter paper as a model of wood was increased by MG treatment after the extraction with alcohol-benzene (1:2) mixture[5]. The extraction ratio is shown in Fig. 6. The extraction ratio was calculated as the ratio of the amount of extractives to the weight of treated filter paper before extraction. Succinic acid (S)-G mixture was used as a reference to MG to investigate influence of the double bonds on both reactivity with cellolose and mechanical properties. Weight gain ratio of MG or anM treated filter paper after the extraction depended on the treatment temperature. When the temperature was at 200 ℃, the extraction ratio was nearly zero. Effective binding of MG to cellulose was confirmed to occur at elevated temperature.

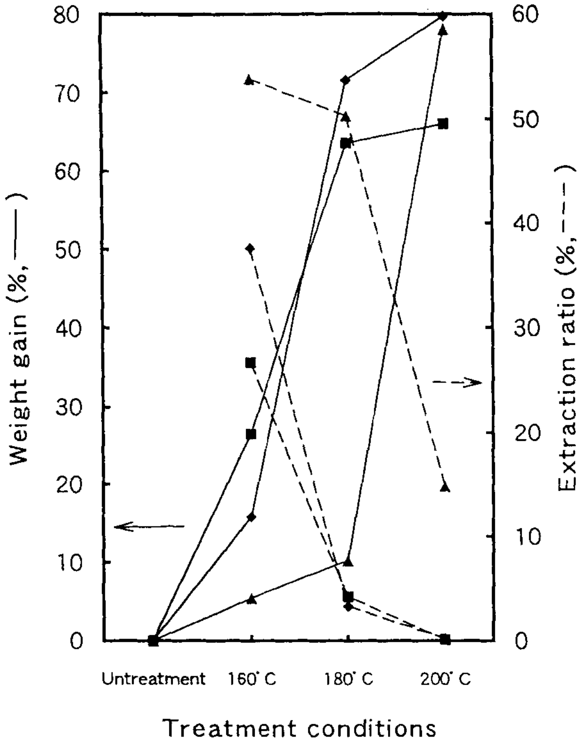


FIGURE 6. Weight Gain and Extraction Ratio of Filter Paper by Heat-Treatment of MG and SG.
Weight Gain of MG1.5(—■—), anMG1.5(—◆—) and SG1.5(—▲—) after Extraction with Alcohol/Benzene.
Extraction ratio of MG1.5(-■-), anMG1.5(-◆-) and SG(-▲-).

^{13}C-CP/MAS NMR spectra of anMG treated cellulose powder was conducted to examine the binding manner between MG and cellulose (Fig. 7). Chemical shifts assigned to carbonyl and vinyl groups were observed as several broad signals at 160-180 ppm and 120-140 ppm, respectively. It suggested that the functional groups did not have individually simple conformation but existed in many circumstances,

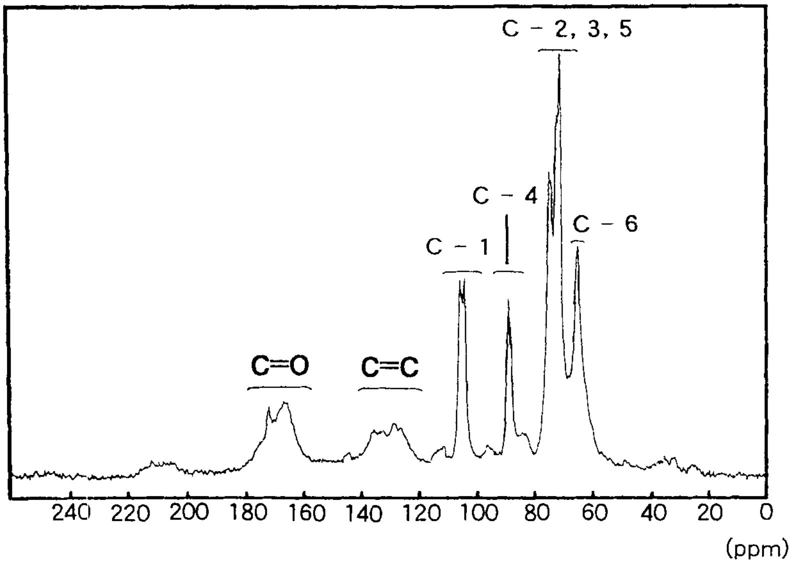


FIGURE 7. ^{13}C-CP/MAS-NMR Spectrum of anMG1.5-Treated Cellulose Powder.

but the results did not prove directly binding patterns. ^{13}C-NMR spectrum of MG treated glucose, the monomer unit of cellulose, was measured in D$_2$O (Fig. 8) to facilitate the analysis with the method of high resolution and the simple model compound. Only two signals of MG at 169 and 172 ppm in Fig. 8(A) assigned to carbonyl groups appeared , but new signal at 170 ppm in the spectrum of MG treated glucose (Fig. 8(B) was observed in addition to the former signals. This clarified the formation of a new ester bond between MG and glucose. Therefore, cellulose seems to be modified by MG to form the ester bonds.

Fate of double bond in M

As mentioned above, it was proved from the results of ^{1}H-NMR that a very small amount of the double bond of M was isomerized to

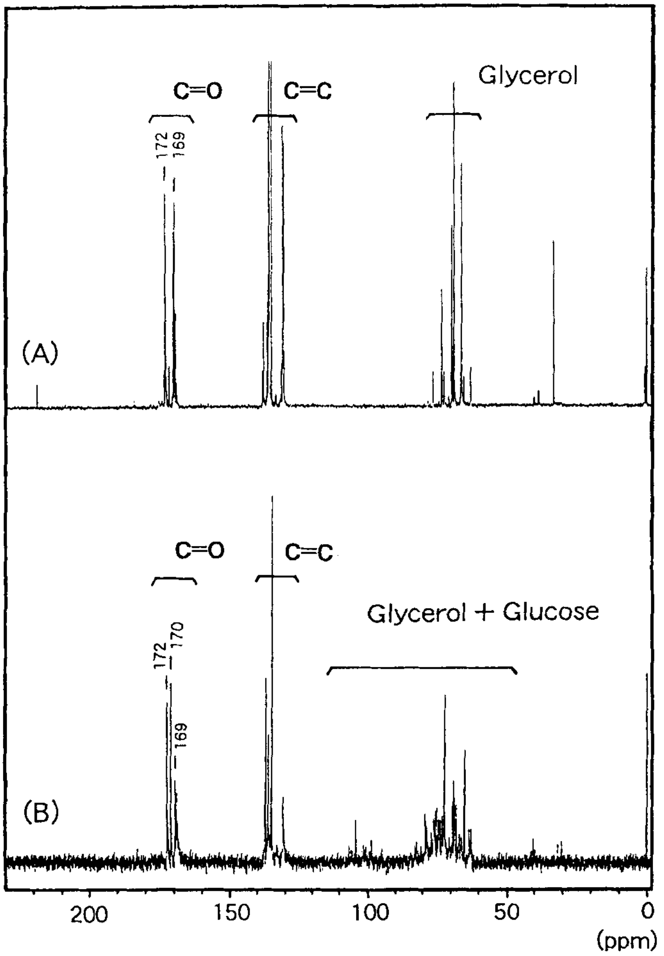


FIGURE 8. ^{13}C-NMR Spectra of anMG3.0 (A) and its Treated Glucose in D_2O.

trans form by the dissolution with heating below 100 °C. As one other reaction of the double bond, polymerization was assumed to occur by heating during the preparation of MG and MG-treated cellulose. Behavior of the double bond was investigated by the titration and IR

TABLE 1

Double Bond Contant After anMG and MG Treatment.

Sample[1]	Double bond Content (nmol)[2]	Ratio of double bond (%)[3]
anMG1.5	1.90	95.0
anMG3.0	1.90	95.1
MG1.5	1.96	97.7
MG3.0	1.95	97.4

[1]: Initial double bond content in sample was 2.00 mmol.

[2]: Determination of double bond in sample after dissolution by the method of Bromate-Bromide.

[3]:

$$\text{Ratio} = \frac{\text{Double bond content in anMG or MG (mmol)}}{\text{Initial Double bond content (mmol)}} \times 100$$

spectra. The titration of double bond using the method of iodine number for that in fatty acid was not applied, because MG and anMG were sparingly soluble in the reagent such as acetic acid and carbon tetrachloride. So the titration was submitted to the method of bromate-bromide using mercury salt as a catalyst, as reported by Lucas et. al.[9]. After the preparation of MG, more than 95% of the double bonds were retained (Table 1). Even if considering this experimental error (5%), the double bonds were still maintained in MG.

Action of the double bond in MG by the reaction of cellulose under the conditions of high temperature was followed by FT-IR spectra. A signal at 1640 cm^{-1} was assigned to the double bond in M, as shown in Fig. 1 and 9, since the peak was not observed in the spectra of both S and G[6]. Each spectrum in Fig. 9 indicates a peak of carbonyl group at 1730 cm^{-1} and that of double bond at 1640 cm^{-1}. The absorbance ratio of double bond to that of carbonyl group was calculated with the base line correction A or B, as shown in Table 2. Since cellulose powders after immersing them in MG solution contained a large amount of water that

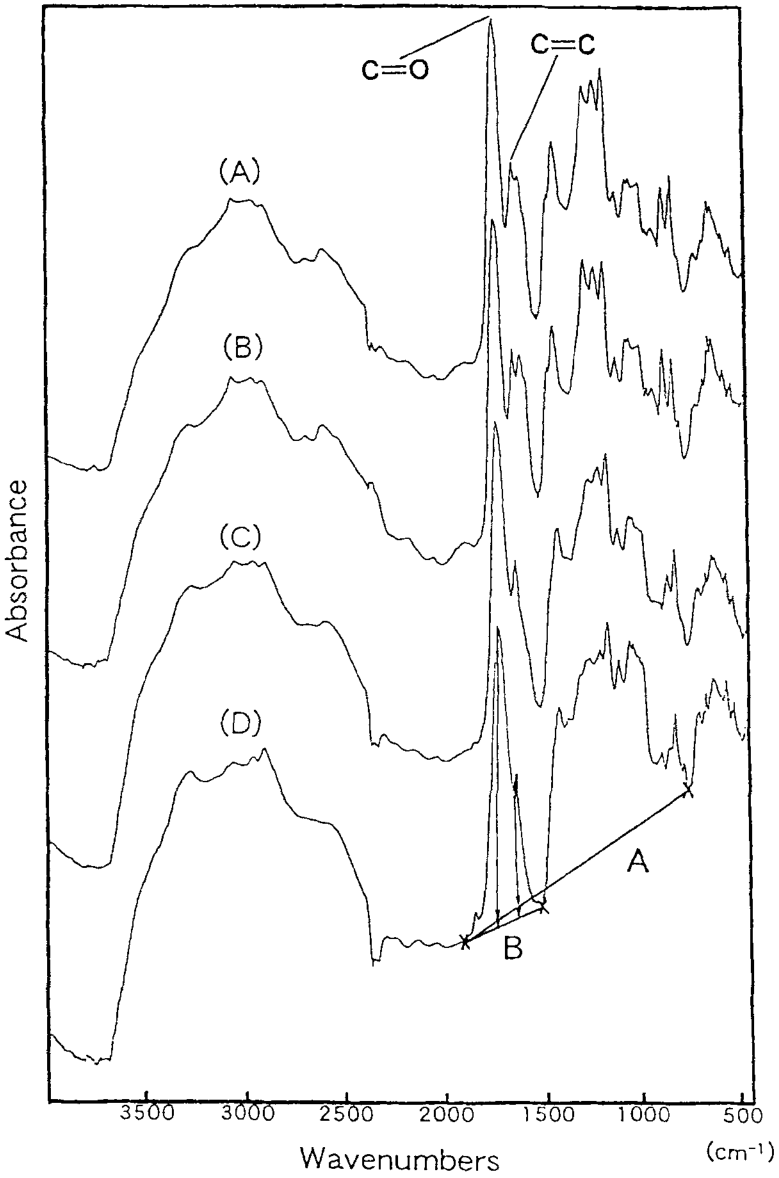


FIGURE 9. FT-IR Spectra of anMG1.5-treated Cellulose Powder by the Method of Diffuse Reflectance.
(A): anMG treated cellulose at 103 °C as control, (B): at 160 °C. (C): at 180 °C, and (D): at 200 °C.

TABLE 2

Absorbance Ratio of anMG Treated Celluloses Before and After Base Line Correction.

Sample		$A_{1640}(C=C)$ / $A_{1730}(C=O)$		
		before correction	Base Line A	Base Line B
anMG1.5 + cellulose	103 ℃	0.74	0.56	0.53
	160 ℃	0.80	0.57	0.54
	180 ℃	0.76	0.52	0.52
	200 ℃	0.76	0.44	0.48
anMG3.0 + cellulose	103 ℃	0.65	0.49	0.47
	160 ℃	0.76	0.57	0.51
	180 ℃	0.75	0.48	0.46
	200 ℃	0.75	0.47	0.48

used for the dilution of MG mixture, the water interfered with quantitative analysis for the IR measurements. After immersion the cellulose powders was heated at 103 ℃ for 5 min to remove the residual water. The resulting powders were regarded as MG-cellulose mixture before heating at elevated temperature and used as a control in this measurement. This experimental error was estimated less than 0.08 if the double bond was not increased by the reaction, because the difference between absorbance of anMG-treated cellulose at 160 ℃ and that of the treated cellulose at 103 ℃ was 0.08. Consequently the double bonds were also not affected by heating during MG treatment for cellulose.

Improvement of water resistance of cellulose by MG treatment

Water resistance of particle boards have been reported to be of cellulose by MG treatment as improvement of water resistance was examined to clarify the relationship of that with molecular size of MG polyesters and with heating temperature under the treatment conditions of cellulose by MG. The equilibrium moisture content at 60% and 86% of relative humidity (RH), at 20 ℃ was plotted against the heating temperature, as shown in Fig. 10. Appearance of water resistance was observed over 180 ℃ at each RH. The heating temperature at 200 ℃ indicated a remarkable effect. However, the dissolution time of M into G showed little effect, suggesting that molecular size of MG was not related to the water resistance.

Improvement of mechanical strength of filter paper by MG treatment

Tensile strength of MG treated filter paper was measured with the same purpose of the water resistance. Effect of MG treatment was not perceived at 160 ℃ of heating temperature as shown in Fig. 11. However, the tensile strength was twice as great on all MG treatments by 180 ℃. Significant increase was observed at 200 ℃ by three times. It has become apparent that improvement of mechanical strength depended on the heating temperature. The molecular size of MG also did not affect the mechanical property. Reinforcement of the tensile strength by MG treatment seems to result from the production of cross-linkages of MG between the chains of cellulose.

Succinic acid (S)-G treatment did not give significant results. Weight gain of SG treated filter papers before and after the extraction in Fig. 6 showed the same level of MG and anMG treated ones. The difference of mechanical strength between SG and MG treatment might be due to the chemical structure of acid component. Therefore, it appeared that the double bonds in M contributed to the improvement of tensile strength.

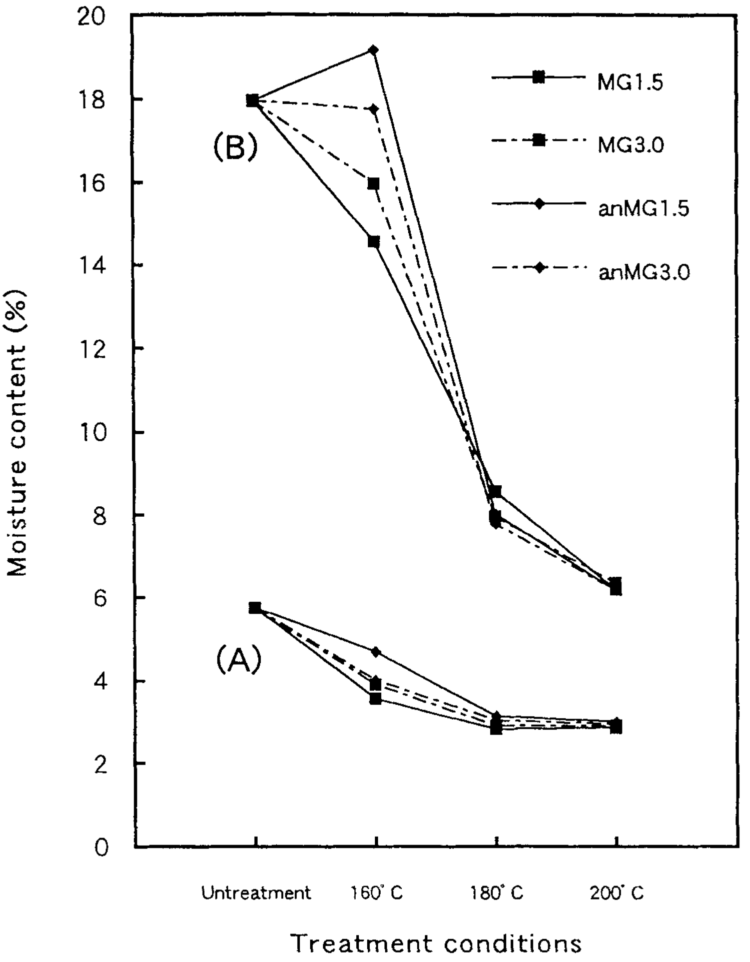


FIGURE 10. Relationship of Heat-Treatment Conditions with Moisture Content of MG-Treated Filter Paper at RH 60% (A) and 86% (B).

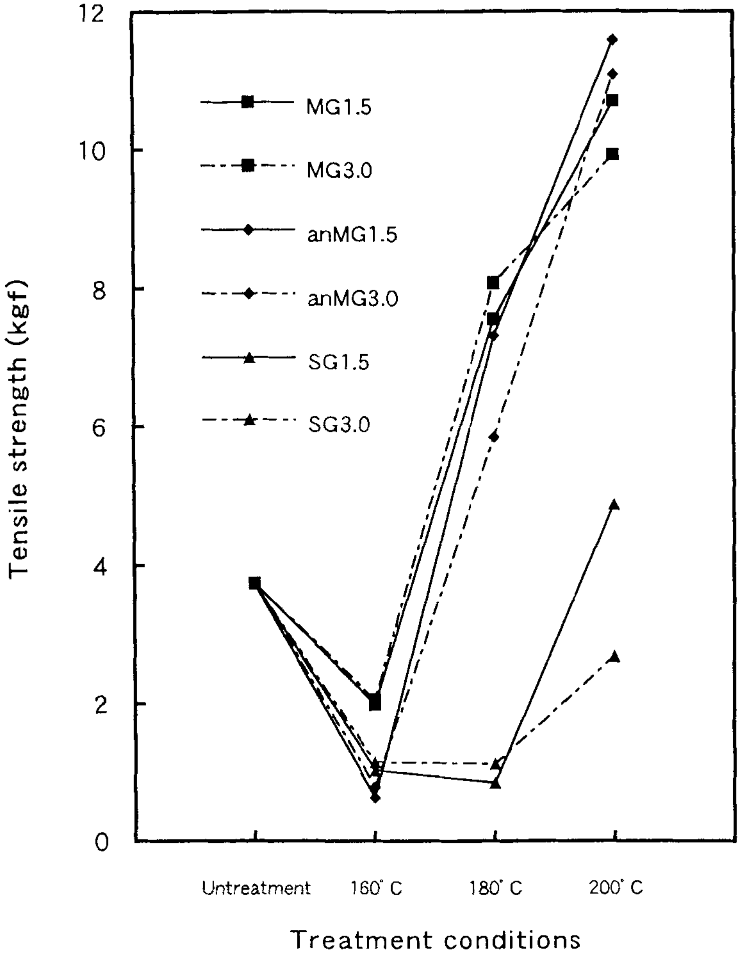


FIGURE 11. Relationship between Heat-Treatment Conditions and Tensile Strengths of MG, anMG and SG-Treated Filter Papers.

CONCLUSION

M and G was reacted during the dissolution under 100 ℃ to form polyesters with more than 1,000 of MW. Furthermore the polyesters of MG were linked to cellulose by the ester bond. Double bonds in M were maintained after the reaction with cellulose.

The molecular size of MG polyesters was not directly related to improvement of either water resistance or the mechanical strength. Appearance of these effects was influenced by the heating conditions during the MG treatment of cellulose. The double bond in M appeared to enhance tensile strength.

Now we plan to investigate effective MG treatments for wood at low temperature.

EXPERIMENTAL

MG mixture solution

Three gram of M was dissolved in 1 g of G in a flask equipped with reflux condenser below 100 ℃ with stirring. To measure acid value and saponification value the solution was evaporated below 40 ℃ for 1 h followed by drying *in vacuo* over night. In addition on the preparation of SG solution, S was dissolved into G at 160 ℃.

MG treated cellulose paper and powder

The MG solution was diluted to 60% with deionized water. Cellulose powder (mesh 100 - 200, Advantec, Japan) and filter paper (diameter 18.5 cm, No. 3, Advantec , Japan) were immersed in the solution for 1 min. After removing the excess solution by filtration, the cellulose samples were heated at 160 °C, 180 °C and 200 °C in oven for 15 min.

Weight gain ratio of MG or SG treated filter paper after extraction of alcohol-benzene (1:2) and extraction ratio were calculated by the following equation:

$$\text{Weight gain (\%)} = \frac{A - B}{B} \times 100$$

$$\text{Extraction ratio (\%)} = \frac{C - A}{C} \times 100$$

where A is Weight of treated filter paper after extraction (g),
B is Weight of intact filter paper (g),
C is Weight of treated filter paper before extraction (g).

Determination of chemical parameters of MG solution

Acid value and saponification value of anhydrous MG solution were measured according to that of fatty acid[10].

Determination of double bond content in MG solution was performed using the bromate - bromide method reported by Lucas[9].

Instrumental analyses

IR spectra of MG treated cellulose were measured using the method of diffuse reflectance on a Bio-Rad FTS-7 FT-IR spectrophotometer.

^{13}C-CP/MAS-NMR spectra were recorded on a Varian MSL-400 spectrometer. ^{1}H-NMR and ^{13}C-NMR were measured on D_2O solution using Jeol EX-270 spectrometer.

MW of MG solution was measured with GFC mode of HPLC system equipped with RI detector using Asahipack GS-220 column at 50 °C. Caribration curve for MW was made using polyethylene glycols and ethylene glycol as standards.

Tensile strength of MG treated filter papers was recorded on a Shimazu NT-303 instrument according to Tappi[11].

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