

Chemical Conversion of Wood to Thermoplastic Material

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Synopsis

A chemically modified wood meal (CE-wood) was prepared by cyanoethylation in the presence of alkaline salts. The temperature T_f at which the wood could flow was measured by a simple mechanical flow tester. The CE-wood demonstrated thermal flow at around 250°C. The T_f value decreased with increasing cyanoethyl content of the wood. Treatment of the wood meal before cyanoethylation with sodium periodate or sodium chlorite lowered T_f . The flow temperature was also decreased by blending the CE-wood with appropriate synthetic polymers or plasticizers. Treatment of CE-wood with chlorine solution was found to be the most effective method of lowering T_f . The T_f value of the slightly chlorinated CE-wood (Cl content=2%) was about 100°C lower than that of the original CE-wood. The lowering of T_f for CE-wood by treatment with chlorine may be interpreted in terms of the plasticizing effect of chlorination on the lignin moiety in the wood.

INTRODUCTION

It is known that thermoplasticity of wood is poor and wood does not thermally flow or melt. If thermal flowability is given to wood, it becomes easy to mold, and may then be useful in a variety of new applications. Recently, Shiraishi and co-workers^{1,2} reported that the wood is converted into thermally meltable materials by esterification or etherification reactions such as caproylation or benzoylation. Modification of cellulose by cyanoethylation has been carried out to improve resistance to rot, heat, and abrasion. Further, cyanoethyl cellulose is useful as a insulating material or dielectrics. It is expected, therefore, that cyanoethylation of wood will result in improvements in characteristics similar to those obtained by cyanoethylation of cellulose.

The purpose of the present work is to elucidate whether thermal flowability is given to wood by cyanoethylation. We have examined the pre-treatment of wood meal and the post-treatment of cyanoethylated wood (CE-wood) in order to developing thermal flowability. The effect of the addition of some synthetic polymers or low molecular weight plasticizers on thermoplastic properties of the CE-wood was also examined.

EXPERIMENTAL

Materials

Wood meal (42–80 mesh) of Buna (*Fagus crenata Blume*) was used after extraction with alcohol–benzene (1:2). Acrylonitrile, low molecular weight plasticizers, synthetic polymers or other reagents were reagent grade and used without further purification.

Cyanoethylation of Wood

Wood meal was steeped for 30 min in a 4% sodium hydroxide solution approximately saturated with sodium thiocyanate or sodium iodine. It was then squeezed out to a wet pickup of 150%. The wet wood meal was quickly placed into a kneader (kneading method), or in a round-bottomed flask (stationary method) and allowed to react with a desired amount of acrylonitrile for a definite period at 40 or 60°C. After the reaction, a slight excess of acetic acid was added to neutralize the alkali catalyst. The product was well washed with water and then dried in vacuum. The product were analyzed for nitrogen content by the Kjeldahl method in order to determine the extent of the reaction.

Pretreatment of Wood Meal with Oxidizing Agents

Wood meal was pretreated with oxidizing agent such as sodium periodate, chlorine solution, or sodium chlorite at ambient temperature for a prescribed time and then reacted with acrylonitrile as described above.

Sodium-Periodate-Treated Wood Meal. One gram of wood meal was treated with 50 mL of sodium periodate solution (25 mmol/L) at pH 3.5 for 24 h and then washed with water and dried in a vacuum.

Chlorine-Treated Wood Meal. One gram of wood meal was treated with 50 mL of chlorine solution (0.2%, w/v) for 3 h under stirring.

Sodium-Chlorite-Treated Wood Meal. One gram of wood meal suspended in 100 mL of 0.2M-sodium chlorite solution containing 1 mL of acetic acid for 30 min under stirring.

Post-Treatment of CE-Wood

The CE-wood was post-treated with chlorine solution, peracetic acid, or hydrogen peroxide.

Chlorine-Treated CE-Wood (Cl-CE-Wood). One gram of CE-wood was stirred with 50 mL of dilute chlorine solution (concentration range of 0.03–0.06%) for a definite period. The chlorinated CE-wood was then thoroughly washed with water and dried in a vacuum. The chlorine content of the product was determined by Schöniger's flask combustion method.³

Peracetic-Acid-Treated CE-Wood. Three grams of CE-wood was slurried by adding it to 30 mL of a solution containing 0.15 g of peracetic acid. The reaction was carried out at 60°C for 2 h.

Hydrogen-Peroxide-Treated CE-Wood. Three grams of CE-wood was treated with 20 mL of 1.62% hydrogen peroxide for 2 h under stirring.

Measurement of Thermal Softening and Thermal Flow Temperature

The thermal softening temperature T_s and thermal flow temperature T_f of the CE-wood was measured using the Koka-shiki Flow Tester Model 301 (Shimazu Seisakusho Co., Japan), as described earlier.⁴ The principle of this device is similar to that of the method previously developed by Goring.⁵ A schematic diagram of a part of flow tester and heating device is shown in Figure 1.

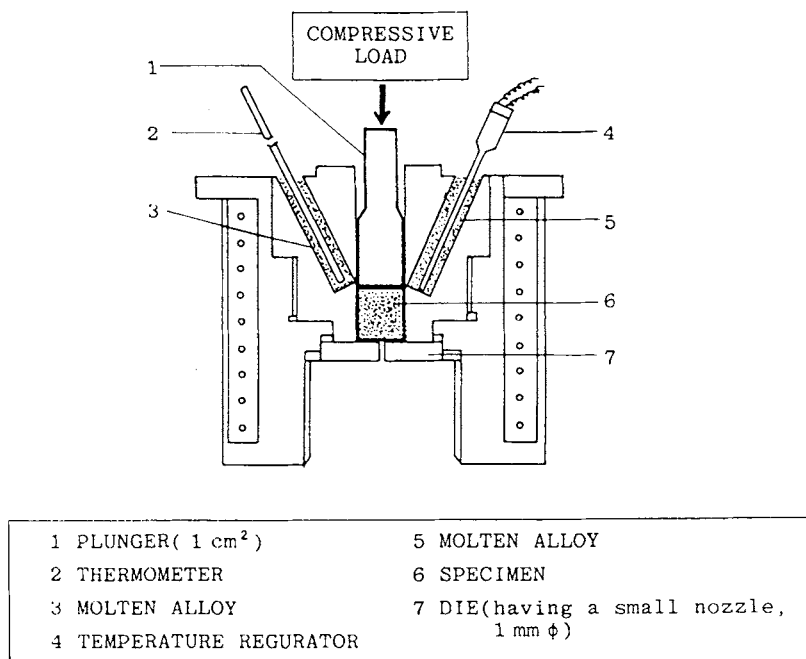


Fig. 1. Schematic diagram of a part of the flow tester.

The wood sample, 0.6–0.8g, was previously molded into cylindrical pellet 10.5 mm in diameter by means of a molding press. The pellet sample was placed in the flow tester. The measurement was carried out at a constant heating rate of 3°C/min and under a constant compressive load of 20 kgf/cm². The temperature range was from 80°C to the flow temperature or to a maximum of 280°C. Compressive deformation of the sample pellet gradually increased with raising temperature. The length of fall of the plunger which indicated this deformation was recorded throughout the experiment.

RESULTS AND DISCUSSION

Effect of Cyanoethylation of Woods on the Thermal Flow

Figure 2 shows the typical thermal behavior for the CE-wood (N content = 9.3%) and original untreated wood meal. The curve of *AB* for the CE-wood corresponds to the softening region where the sample is gradually being deformed by a compressive load, and the small void space in the sample is being reduced. A region, *BC*, is then reached where the position of the plunger varies much less with temperature. Further increase in temperature then leads to the flow region, *CD*, where the sample obviously flows through a nozzle placed at the bottom of the cylinder. The plunger fall velocity was computed in mm per min. When the plunger fall velocity was plotted against temperature, two peaks were found corresponding to the softening temperature T_s and the flow temperature T_f , respectively. T_s and T_f values of the CE-wood sample were found to be 127 and 254°C, respectively. As shown in Figure 2, untreated wood meal was somewhat

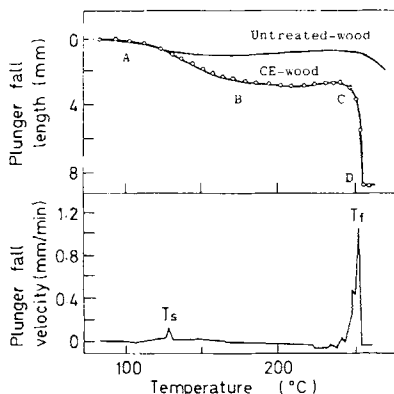


Fig. 2. Thermal softening and flow curves for CE-wood and untreated wood meal.

deformed at elevated temperature, but did not undergo thermal flow.

Preliminary tests were made of the effect on T_f of the water content of the wood samples. An increase in the water content showed little effect on the T_f . For example, the T_f values of 265, 266, and 264°C were found for CE-wood samples with water contents of 0%, 6.1%, and 12.8%, respectively. Therefore, air-dried samples which contained less than 5% water were used for the measurement of thermal flow.

The effect of addition of salts (swelling agent) on cyanoethylation of wood meal is shown in Table I. These samples were prepared by the stationary method. If wood was pretreated in a sodium hydroxide solution at a concentration of 20%, the nitrogen content of the reaction product was low. This low value was probably due to the cleavage of the cyanoethyl/cellulose bonds by the strong alkali used. However, neutral swelling agents such as sodium thiocyanate, sodium iodine, and potassium iodine in conjunction with dilute alkali increased accessibility of wood substrate and resulted in high nitrogen content of the CE-wood (N content = 9–10%). Further, the more than 85% of the original wood meal was recovered. These high nitrogen content samples show thermal flow at about 270°C.

The effect of nitrogen content of the cyanoethylated woods on the thermal flow temperature is shown in Figure 3. The samples prepared by the stationary method were obtained by reacting wood meal with acrylonitrile in

TABLE I
Effect of Addition of Salts on the Cyanoethylation of Wood^a

Concn NaOH (%)	Swelling salt	Temp (°C)	Time (h)	Nitrogen content (%)	Recovery of wood (%)	T_f (°C)
20	—	55	2	2.5	—	—
4	—	40	3	5.8	85.4	—
4	Na-SCN	40	3	9.9	87.9	275
4	NaI	40	3	9.8	89.3	271
4	KI	40	3	9.0	89.0	267

^a The cyanoethylated woods were prepared with 2.3 mL acrylonitrile/g wood meal by the stationary method.

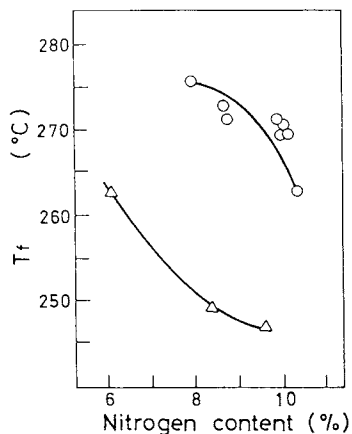


Fig. 3. Effect of nitrogen content on the T_f of the CE-woods prepared by the stationary method (○) and by the kneading method (△).

the flask on standing, while the samples prepared by the kneading method were obtained by the reaction in the kneader with stirring. The T_f of both samples lowered with increase in the nitrogen content of the CE-wood. T_f of the kneading method was 20°C lower than that of stationary method samples at the same nitrogen content. The lower T_f in the case of kneading samples may be due to the more uniform distribution of cyanoethyl group in the wood meal particles.

Effect of Pretreatment of Wood Meal

In order to lower the T_f of the CE-wood, the wood meal was pretreated with oxidizing agents and then subjected to the reaction with acrylonitrile in the manner described above. It should be noted that very little of the lignin is removed by the pretreatment of the wood meal. The T_f and the nitrogen content of the CE-wood samples are shown in Table II. The nitrogen content of the CE-woods made by the pretreatment process were comparable to that of the control CE-wood except for the sample pretreated by chlorine solution. In the case of the pretreatment with chlorine, the nitrogen content of the CE-wood was somewhat low. This may be due to the poor wettability of the chlorinated wood by the cyanoethylation reaction medium. The T_f of the CE-wood which were prepared by pretreatment with sodium chlorite and/or sodium periodate, followed by cyanoethylation, were found to be about 20°C lower than that of control sample. In the case of CE-wood prepared from the chlorinated wood, T_f was comparable to that of the control, even though the nitrogen content was lower. It seems that thermal property of CE-wood is enhanced by chlorination of a starting wood meal.

TABLE II
The T_f values and Nitrogen Contents of CE-Woods Prepared from Pretreated Wood Meal

Treatment	Untreated	NaIO ₄	Cl ₂	NaClO ₂	NaIO ₄ + NaClO ₂
N (%)	9.9	9.3	7.0	9.8	10.1
T_f (°C)	272	254	270	253	250

Effect of Blending of Some Synthetic Polymers or Low Molecular Weight Plasticizers

Experiments were then carried out to determine whether or not the thermal properties of the CE-woods were enhanced by blending with some synthetic polymers or low molecular weight plasticizers. These results are shown in Table III. The T_f value of the CE-wood containing tricresyl phosphate decreased to 232°C, whereas that of original CE-wood was found to be 246°C. Similarly, the T_f of the CE-wood containing polyethylene glycol was found to be 231°C. But, the addition of the other plasticizers such as *N*-butyl maleate, dimethyl phthalate, or tributyl phosphate had little effect on T_f .

The plasticization of the CE-wood with polystyrene, poly(methyl methacrylate), and high density polyethylene was effective, and for their samples the T_f values were about 20°C lower than that of the original CE-wood.

Effect of Post-Treatment of CE-wood

Shown in Table IV are the T_f values of the CE-wood treated with peracetic acid, hydrogen peroxide, or chlorine solution. For post-treatment with peracetic acid, T_f agreed very closely with that of the original CE-wood. In the case, the thermal properties of the CE-wood were not changed. On the other hand, the treatment with hydrogen peroxide increased the T_f to 268°C. This may be due to the formation of carbamoylethyl groups by the hydrolysis of cyanoethyl groups in the presence of alkaline hydrogen peroxide. Such groups would tend to form intermolecular hydrogen bonds within the wood structure.

In the case of post-treatment with chlorine, T_f decreased markedly. The changes in the plunger fall length and its fall velocity for the treatment of the CE-wood with chlorine solution are shown in Figure 4. For the chlorine-treated sample, the plunger fall length corresponding to the softening region was large, and the plunger fall velocity was sharper than that of the original CE-wood. The flow region, in which the sample flows through the nozzle,

TABLE III
Effect of the T_f of CE-Wood of Blending with 10% of Some Synthetic Polymers or Low Molecular Weight Plasticizers

Additive	T_f (°C)
Control CE-wood	246
Plasticizer	
Tricresyl phosphate	232
<i>n</i> -Butyl maleate	248
Tributyl phosphate	242
Dimethyl phthalate	247
Polymer	
Poly(ethylene glycol) (MW = 300)	231
polystyrene	225
poly(methyl methacrylate)	223
high-density polyethylene	226

TABLE IV
Effect of Post-Treatment of CE-Wood with Various Oxidizing Agents

Post-treatment	Control	CH ₃ COOOH	Cl ₂	H ₂ O ₂
N (%)	9.6	9.8	9.3	9.7
T _f (°C)	256	254	152	268

was narrow for the chlorine-treated sample with a temperature range of 1–2°C. Thus the T_f peak in the velocity curve was sharper than that of the control as shown in Figure 4. It was, therefore, easy to determine the T_s and the T_f .

Effect of Changes in Treatment Variables in the Procedure for Chlorination of CE-Wood

As demonstrated above, the thermal flowability of the CE-wood was improved considerably by the treatment with chlorine. The effects of the treatment of the CE-wood with chlorine on T_s or T_f were examined in more detail.

Chlorine Dosage. The effect of the amount of chlorine dosage to the sample on the combined chlorine and the thermal behavior are shown in Figure 5. The experiments were carried out with different concentrations of chlorine solution at a liquor to sample ratio 50:1 for 3 h. The amount of the combined chlorine increased with increase in the amount of chlorine dosage, but it leveled off around 30% (30 g Cl/100 g CE-wood). The decrease in nitrogen content could be accounted for approximately by the increase in sample weight due to the addition of the chlorine. The flow temperatures were lowered with increase in the amount of chlorine dosage, but T_f never went below about 140°C even at a chlorine dosage of 10% or above. It is clear that the decrease in T_f is rapid at chlorine dosages below 10%. How-

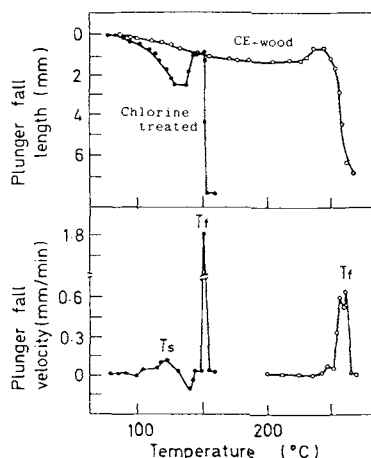


Fig. 4. Thermal softening and flow curves for CE-wood treated with chlorine.

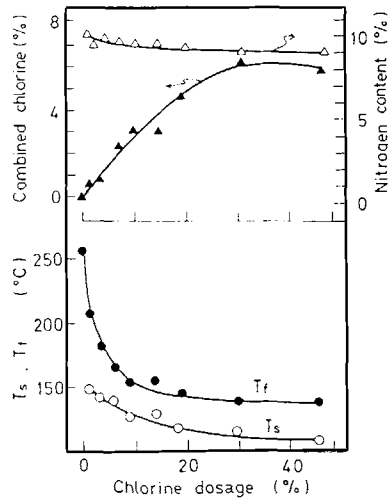


Fig. 5. Effect of amount of chlorine dosage to CE-wood on chlorination and thermal behavior of CE-wood.

ever, further addition of chlorine shows comparatively little effect on the T_f .

Time of Treatment. Figure 6 shows the effect of time of treatment with chlorine solution at a constant chlorine dosage of 10% on T_f and T_s . At the first measurement point of 30 min T_f had already decreased to 150°C. Longer treatment time had no effect on T_f . The T_s values tended to increase slightly after 3 h of treatment.

The relationship between the amount of the combined chlorine and the degree of lowering of T_f from that of the original CE-wood, ΔT_f , is shown in Figure 7. The ΔT_f value increased rapidly to about 100°C with an increase in the amount of combined chlorine up to about 2%. At higher levels of chlorination, ΔT_f increased more gradually. It is clear that only small

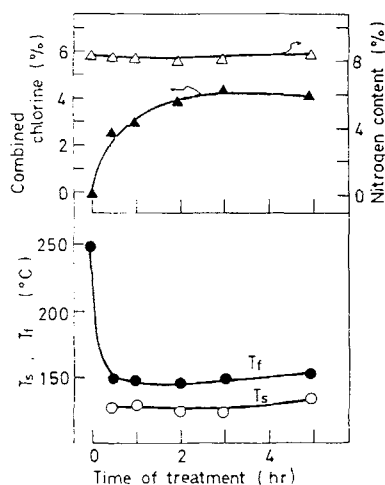


Fig. 6. Effect on T_s and T_f of time of treatment of CE-wood with chlorine solution at a constant chlorine dosage (10%).

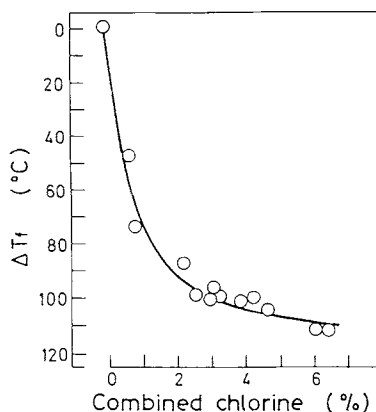


Fig. 7. Relationship between the extent of chlorination of CE-wood and the degree of lowering of T_f .

amounts of chlorine combined to wood substrate are necessary for the lowering of the T_f of the CE-wood.

It is well known that when wood is chlorinated under mild condition, chlorine atoms are introduced mainly into the aromatic nuclei of lignin.⁶ Thus, the lowering of the thermal flow temperature for cyanoethylated wood treated with chlorine may be interpreted in terms of the effect of plasticization caused by the chlorinated of the lignin macromolecule in wood. If this reasoning is correct, T_f of CE-wood should be lowered by other halogenation or nitration reactions with the nuclei of the lignin. Moreover, the T_f of other chemically modified woods should be lowered by treatment with chlorine.

TABLE V
Effect of Chlorination, Bromination, or Nitration of Chemically Modified Woods on Their T_f Values

Sample	Treatment	Combined to wood (%)	T_f (°C)
Cyanoethylated wood (N: 9.2 %)	—	—	259
	Chlorination	Cl: 3.7	155
	Bromination	Br: 4.1	165
Cyanoethylated wood (N: 9.6%)	—	—	248
	Nitration ^a	NO ₂ : 6.9	171
Benzylated wood ^b	—	—	250
	Chlorination	Cl: 4.4	133
Hydroxyethylated wood ^c	—	—	—
	Chlorination	Cl: 2.1	167

^a Nitration was carried out by treating wood for 6 h at 0°C with a mixture containing 20% fuming nitric acid, 24% acetic anhydride, and 56% CCl₄.

^b Benzylated wood was prepared by treating wood with 30% NaOH, and then pressing and reacting the wood with benzyl chloride for 6 h at 90°C.

^c Hydroxyethylated wood was prepared by treating wood with 18% NaOH, and then pressing and reacting the wood with ethylene oxide under reduced pressure for 18 h.

Accordingly, the CE-wood was treated with 0.2% (w/v) of bromine solution or with fuming nitric acid. Benzylated wood and hydroxyethylated wood were prepared and these samples were treated with chlorine solution. The effect of the treatment of these samples on their T_f are shown in Table V. The T_f value for the brominated CE-wood was found to be 165°C at a bromine content of 4.1%, whereas that of the original CE-wood was found to be 259°C. Similarly, the T_f of the nitrated CE-wood which contained 6.9% of nitrate groups decreased to 171°C. The T_f for benzylated wood was lowered to 133°C by chlorination. The hydroxyethylated wood did not show thermal flow, but after chlorination the T_f value was found to be 167°C.

From the above results, it is concluded that the thermal flowability of some chemically modified woods is significantly improved by introduction of appropriate functional groups to wood components, particularly to the lignin in the wood.

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