

Wood-Phenol Adhesives Prepared from Carboxymethylated Wood. I*

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Synopsis

Preparation of carboxymethylated wood (CM wood)-phenol resin adhesives has been attempted by two methods, "kneading method" and "solvolysis method," and their adhesion strength has been studied. The two preparation methods differ in the dissolution step. In the case of the kneading method, CM wood was dissolved in aqueous phenol by kneading at 100–120°C under shear, whereas, in the case of the solvolysis method, the dissolution was facilitated by phenolysis at 80°C in the presence of appropriate amounts of hydrochloric acid. The wood-based adhesive prepared by the solvolysis method revealed excellent and enhanced applicability compared with that of the adhesive prepared by the kneading method, although the latter can be used as an adhesive for wood. Adhesion strength of these adhesives was enhanced when poorly substituted CM wood and appropriate amounts of formaldehyde were used in the resin preparation. A crosslinking agent for carboxymethyl cellulose, that is, polymeric MDI, was also added just before application. The water-proof adhesion strength was higher than the JIS specification for phenol resin adhesives for this modification.

INTRODUCTION

Several attempts have hitherto been made to utilize a part of wood, that is, a certain wood component as adhesives. Representative examples are tannin-formaldehyde resin adhesives and lignin-phenol resin adhesives. Cellulose can also be converted to adhesives by derivatization. However, feasibility of chemically converting whole wood to adhesives is seldom explored except in a few of our previous works.^{1,2} This is chiefly because of the fact that the method to confer thermofluidity or dissolvability to wood was not known. We have, however, found a novel procedure to chemically convert wood into plastic-like materials, and this has made it possible to prepare the new wood-based adhesives.

In our previous report,¹ preparation of water-soluble adhesives, which were made by mixing soluble carboxymethylated wood (CM wood) in phenols as well as formalin, and applied therefrom, has been described. CM wood was first dissolved in phenols by mixing in a Labo-plastomill (kneader), then formalin was added, and the whole solution was resinified to obtain aqueous adhesives with wood as a major component. These workable, pastelike adhesives showed satisfactory performance as far as the dry bond strength was concerned. So, as a continuation of the investigation, it was necessary to study in detail the adhesive properties of the above products. Thus, the present investigation is aimed to make it clear that our novel wood-based

*Parts of this study were presented at the 34th National Meeting of Wood Research Society, Japan (April 1984).

adhesives would perform satisfactorily, possess an enough waterproof glueability, and would be good prospects in opening a new field of commercial adhesives.

As described in our previous report, adhesion tests have been made with test specimens of 30(L) × 25(R) × 10(T) mm, by measuring compression adhesive strength under shear. This kind of testing for adhesives, which need high temperature for their curing, causes several problems. For example, use of considerably high hot-press temperature, obscures optimum curing time, etc.

Comparison with the already published data of glueability of the commercial adhesives is also not possible. In that sense, investigations utilizing thin veneer-type specimens (usually used in making plywood) and testing of the shear adhesive strength by tension loading are more desirable. A related investigation using such testing is also in progress and will be reported in the near future.

However, as mentioned above, the present testing procedure involves a thick test specimen, which forces us to use severe curing as well as severe waterproof test conditions. Thus, as the result, the difference in adhesion strength becomes more prominent. This kind of unusual and severe testing procedure can be considered as an effective method in evaluating improvement due to the novel adhesives.

EXPERIMENTAL

Materials

Makanba (birch: *betula maximowiczii* Regel) sap-wood meal (cold water extracted) was used for carboxymethylation. All the chemicals and solvents used were of "extra-pure" grade or "guaranteed reagent" grade and were used without purification. As a crosslinking agent, polymeric MDI (4,4', diphenylmethane diisocyanate; Oshika Shinko Co. Ltd. H-3M) was used.

Carboxymethylation

Carboxymethylation of wood was carried out in accordance with the conventional method using isopropanol as the solvent.^{1,3} That is, a wood meal sample (75 g) was suspended in 1875 mL of isopropanol in a 2 L separation flask, and stirred for about 10 min after closing the lid tightly. The stirring was continued throughout the reaction. Then, 30 wt% aqueous sodium hydroxide containing 60 g of solid was added to the flask dropwise over a period of 30 min. After the addition, stirring was continued for 1 h and an isopropanol solution (90 mL) containing 90 g monochloroacetic acid was added dropwise for 30 min. After the addition of all of the reagents, the reaction was continued at 55°C for 3.5 h. Carboxymethylation was also conducted using one third or one fourth amount of sodium hydroxide as well as monochloroacetic acid used in above-mentioned standard procedure. Thus, CM woods with lower degrees of substitution were prepared. After completion of the reaction, the supernatant liquid was decanted, the reaction product was washed with 70% aqueous methanol, neutralized with dropwise addition of 90% aqueous acetic acid, poured into a large excess

of 70% aqueous methanol, washed with methanol, collected by filtration using G-2 sintered funnel, dried, weighed, and the weight increase (WI) of the sample was calculated.

IR Analysis

IR spectra of the CM woods were measured on a Hitachi EPI G-3 diffraction grating infrared spectrometer by using the KBr pellet method. The absorbance ratio of the key bands was determined by the base-line method.

Preparation of CM Wood-Phenol Adhesives or CM Wood-Resorcinol Adhesives through Kneading ("Kneading Method")

CM wood was brought to a pastelike state by mixing with a small amount of water using Irie Shokai, Table-top type, kneader PBV-0.1 or Toyo-Seiki Labo-Plastomill LPM 18-125. Then, resinification with phenol⁴ or resorcinol⁵ was attempted by respective conventional methods using the pastes. The detail preparation methods are as follows:

1. CM Wood-Phenol Adhesives. Ten wt parts of CM wood and 2 wt parts of water were mixed at 100°C in a kneader obtaining a slurry. Then, 10 wt parts of phenol and 0.5 wt parts of 50% aqueous sodium hydroxide were added dropwise and mixed under shear at 120°C for 30 min, where mixing was carried out in an open system allowing to evaporate the excess water. At the end of the mixing stage, the temperature was lowered to 80°C and 13 wt parts of formalin (35% aqueous formaldehyde) were then added. Methylation and partial condensation proceeded for 3 h at this temperature with mixing under shear. Pastelike prepolymers were obtained. The products were diluted to twice the volume with water and cooled to room temperature under mixing. Further, 2 wt parts of 50% aqueous sodium hydroxide was added to the diluted product, and the resulting solution was used as adhesive material.

2. CM Wood-Resorcinol Adhesives. Ten wt parts of CM wood and 10 wt parts of resorcinol were mixed in a kneader at 120°C for 30 min; 1.7 wt parts of water was added dropwise so as not to decrease the shear torque of kneading rapidly. After addition of water, the mixing was continued for 5 min. Then, the temperature was lowered to 60°C, and 0.7 mol of formaldehyde per mole of resorcinol was added dropwise as formalin. Methylation and the condensation reaction were allowed to proceed at 60°C, for 2 h with mixing under shear. Pastelike prepolymers were obtained, and appropriately diluted to get the intended concentration of adhesive. Just prior to application, a definite amount of formalin as the hardner was added to make the molar ratio of resorcinol to formaldehyde to 1:2 in the final product.

Dissolution of CM wood into Phenols Facilitated by Phenolysis and Their Resinification to Prepare Adhesives ("Phenolysis Method")

As CM wood was found to dissolve well into phenol under the conditions which lead to phenolysis of lignin in wood, CM wood-phenol resin adhesives were prepared by aiding the dissolution process by phenolysis. The typical dissolution process involves melting of phenol in a 100 mL separation flask

at 50°C followed by addition of aqueous hydrochloric acid and thoroughly mixing the contents. To the above solution CM wood was added, the flask was closed, and the contents were stirred at definite temperature for a definite time. However, it was necessary to alter the amount of hydrochloric acid, dissolution temperature, and time depending upon the degree of substitution of CM wood.

1. Dissolution of CM Wood Prepared by Using a Standard Amount of Etherifying Agent. The weight ratio of CM wood to phenol was 1:1. The amount of hydrochloric acid was 14 wt % of phenol. The dissolution temperature and time were 80°C and 1 h, respectively.

2. Dissolution of CM Wood Prepared by Using One Third of the Standard Amount of Etherifying Agent. The weight ratio of CM wood to phenol was 1:1, that is, same as in the above case but the amount of hydrochloric acid was increased to 16 wt % of phenol and dissolution was achieved by stirring the contents at 80°C for 2.5 h.

3. Dissolution of CM Wood Prepared by Using One Fourth of the Standard Amount of Etherifying Agent. CM wood and phenol in 1:1 weight ratio and in the presence of 18 wt % of hydrochloric acid, based on phenol, were stirred at 120°C for 2.5 h to obtain a paste.

The solutions or pastes thus obtained were then neutralized by dropwise addition of 50% aqueous sodium hydroxide solution. Then, the solutions were converted to phenol resin adhesives in reference to the procedure reported by Nakarai and Watanabe.³ That is, after dropwise addition of 50% aqueous sodium hydroxide solution to the above wood solutions until their pH became 9.0, formalin, 33.1 or 49.1 mL (molar ratio of 1.4 or 2.1 based on phenol) was added, and the methylation and the partial condensation were allowed to proceed under constant agitation at 85–90°C for 3 h to get a precondensation product of phenolic resin. To the prepolymer (resin solution), 50% aqueous sodium hydroxide was added until the pH of the resin solution became 11 and stirred for several minutes to obtain a solution-type adhesive.

Furthermore, 20% of the amount of phenol was replaced by resorcinol, and the corresponding phenol resin adhesive was prepared. In this case, dissolution was also facilitated by phenolysis under the same conditions as described in the above section.² The amount of formaldehyde was 2.1 molar ratio based on that of phenols. The duration of prepolymer formation was 1 h and the pH of resulting prepolymer resin solution was adjusted to 9 and used as an adhesive.

Improvement of Water Resistance of Adhesives by Crosslinking

Polymeric MDI (4,4'-diphenylmethane diisocyanate) was used as a crosslinking agent. The crosslinking agent, 20 parts, was added to 100 parts of CM wood-phenol resin adhesives and blended well just before use to improve water resistance of the adhesives.

Adhesion Tests

Wood specimens (Makanba edge grain cut) of 30(L) × 25(R) × 10(T) mm size were glued together using 25(L) × 25(R) mm surface as the gluing area. The amount of adhesive used ranged from 320 to 370 g/m².

After cold-pressing for 1 h under a pressure of 10 kgf/cm², curing was achieved by hot-pressing the test specimens under 15 kgf/cm² pressure at definite temperatures for definite periods, followed by cold-pressing at room temperature under the same pressure. Shear strength adhesive tests were performed by compression loading according to the Japan Industrial Standard (JIS) K-6852 for phenol resin adhesives, to evaluate dry bond strength. On the other hand, in order to evaluate water proof adhesion strength, glued specimens were subjected to the "boil-dry-boil" cycle test. That is, the test specimens were placed in boiling water for 4 h, dried in an air-circulated oven at 60°C for 20 h, reintroduced in boiling water for 4 h, cooled by immersing in cold water (20°C), and tested in the wet state for shear adhesive strength as mentioned above.

The number of test specimens for each testing was five.

Measurement of Glue-Line Temperature During Hot Pressing

Since the adherends were quite thick, it was thought to be necessary to determine the actual temperature at glue line during hot pressing. For this purpose, a copper-constantan thermocouple was inserted into the center of the glue line and the temperature change was recorded throughout the pressing time using a multichannel digital recorder (Takada Riken Ltd.).

RESULTS AND DISCUSSION

Carboxymethylation of Wood

Results of characterization of CM wood prepared by using different quantities of etherifying agents are shown in Table I. From the table, the degree of the etherification is known to decrease with a decrease in the quantity of monochloroacetic acid added. The appearance of the CM wood meal does not differ from that of untreated wood meal even though carboxymethylation was conducted with the largest amount of the etherifying agent (the standard method) as shown in Figure 1.

Water solubility of these three CM wood formulations is found to increase with an increase in the degree of etherification. From the CM wood meal with the highest water solubility, an etherified wood-based phenol resin adhesive was prepared using the kneading method and its gluability was examined.

TABLE I
Effect of the Amount of Etherifying Agent (Monochloroacetic Acid and Sodium Hydroxide) on the Carboxymethylation^a

Sample	ClCH ₂ COOH (g/g wood)	Weight increase (%)	A_{1600}/A_{2925}
A-1	1.2	43.7	9.185
A-2	0.4	29.1	5.254
A-3	0.3	0.07	2.741

^a Extent of carboxymethylation was determined by WI and IR absorption ratio of —OH/—C=O.

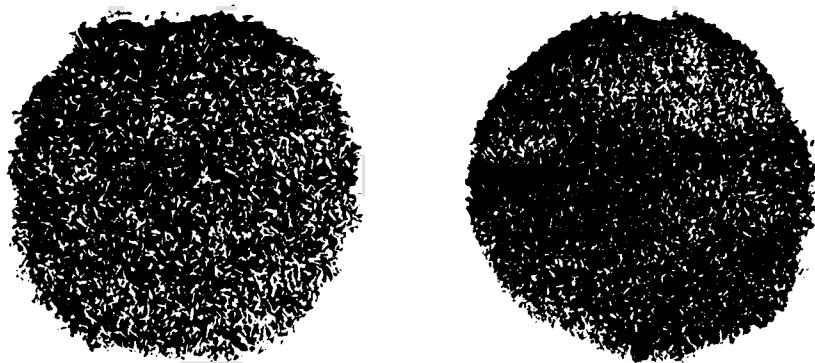


Fig. 1. Untreated wood (left) and CM wood prepared by using the standard amount of etherifying agent (right).

Adhesives from CM wood by the Kneading Method

The CM wood can considerably be converted to a pastelike solution only by kneading at 100°C. Thus, further kneading after adding phenol and formalin to the system and resinification in the presence of sodium hydroxide catalyst resulted in a red-brown paste. In this case, although a slight undissolved wood remained in the paste, it did not impair its workability. Thus, CM wood-phenol resin prepolymer prepared in this way can, successfully, be used as an adhesive. The compression shear adhesive strength of the specimens glued at 130°C is shown as a function of hot-pressing time in Figure 2. The adhesive strength for the samples with hot-pressing time of 15 min exceeded 100 kgf/cm², that is, the Japan Industrial Standard (JIS) specification for phenol resin adhesives. Further increase in the hot-pressing time did not show any change in the adhesive strength. Since the adherends are quite thick (1 cm), it is plausible that the rate of heating at glue line is fairly slow and as a result the apparent leveling-off temperature or the temperature after the necessary hot-pressing time at the glue line will be considerably lower than the hot-press temperature. Therefore, the actual glue-line temperature was measured by maintaining the hot-press temperature at 130°C and the results are shown in Figure 3. As can be seen from the figure, the glue line temperature can only reach to 89°C in 15 min, 91°C in 20 min, and 95°C in 25 min. Usually, phenol-formaldehyde resins require 130–150°C temperature for 3-dimensional curing. This means, in the present case, a complete curing of the adhesive can not be expected to take place. Therefore, the adhesive strength observed in Figure 1 can be attributed to curing through a solvent release mechanism. That is, water, unreacted phenol, and formaldehyde or their low molecular weight reaction products either penetrate the test specimens (adherends) or evaporate off leaving behind high molecular weight wood components in the glue line, thus giving excellent dry bond adhesive strength.

This argument could be confirmed by three kinds of following experiments. First, when above samples were subjected to a "boil-dry-boil" cycle test to evaluate wet adhesive strength, delamination occurred during the first boil, indicating the incomplete 3-dimensional cure. Second, commercial phenol-formaldehyde adhesive was used to glue wood adherends under

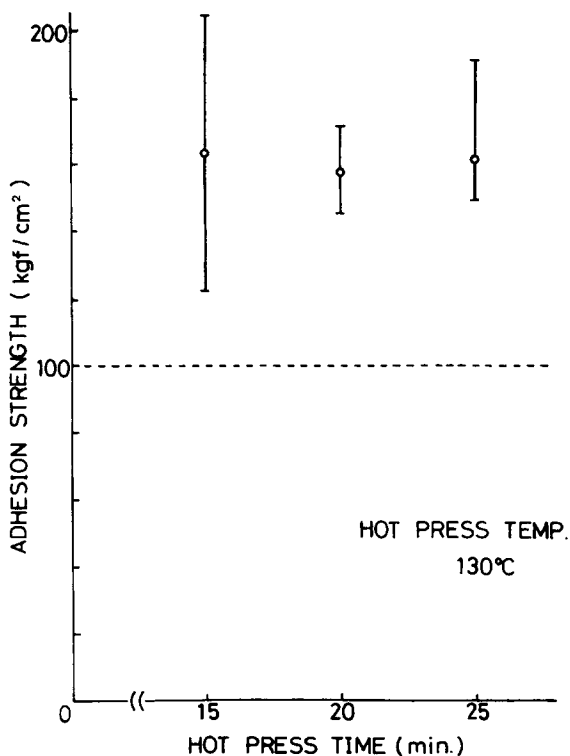


Fig. 2. Dry bond strength of CM wood-phenol resin adhesive prepared by the kneading method. CM wood was prepared by using the standard amount of etherifying agent; CM wood to phenol = 1:1 (wt).

almost the same adhesion conditions and the waterproof adhesion strength was also examined. In this case, the delamination occurred during the first or second boil. Third, CM wood was kneaded to obtain an aqueous paste, and the paste was used as an adhesive, although its workability was not very good. Results of adhesion tests with this aqueous paste adhesive are shown in Table II. Here, the hot-press temperatures of 80, 100, and 130°C and hot-press times of 15–40 min were used. It can be seen from the table that the adhesive strength can exceed the JIS demand for phenol resin adhesives when gluing time was sufficient. This adhesive is not expected to cure by chemical setting but by a solvent-release mechanism.

These facts, very clearly, indicate the incomplete curing of resol type adhesives at hot-press temperature of around 130°C in this experiment. In that sense, it is necessary to adopt higher hot-press temperatures so as to complete the 3-dimensional curing of the adhesive and to evaluate the wood-based adhesives. This point will be discussed in later sections.

By kneading a mixture of CM wood and resorcinol, similar aqueous resorcinol adhesives were also prepared. These adhesives showed greater workability compared with that of CM wood-phenol resin adhesives. No undissolved wood meal was detected in the paste.

The compression shear adhesive strength of the specimens glued at 80–130°C is shown as a function of hot press time in Figure 4. Regardless of

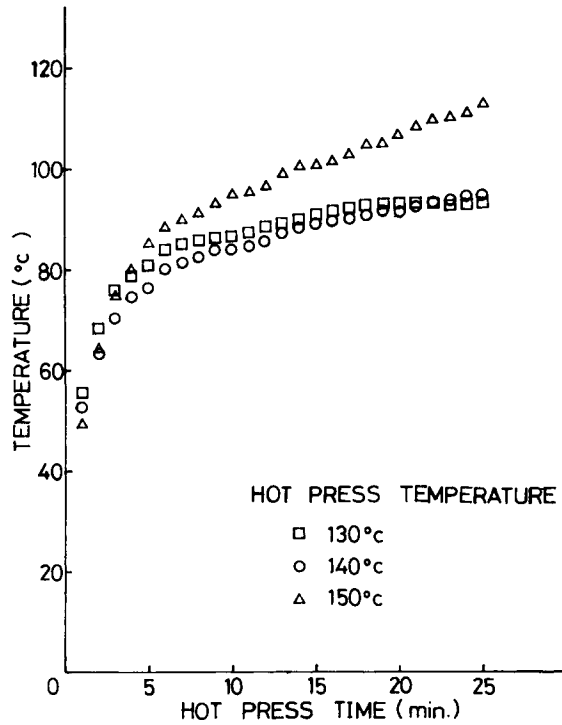


Fig. 3. Change in glue-line temperature with hot-press time. Thickness of adherend: 10 mm; hot-press temperature: (□) 130°C; (○) 140°C; (△) 150°C.

the hot-press temperature, the adhesive strength was found to exceed 100 kgf/cm², that is, the JIS specification for phenol resin adhesive, after sufficient time of hot pressing. When the hot-press temperature of 130°C was used, the adhesive strength exceeded the JIS demand in less than 15 min of hot pressing. The actual glue line temperatures were also measured as a function of hot-press time for each hot-press temperature used. The results are shown in Figure 5.

TABLE II
Dry Bond Strength of Aqueous CM Wood Paste Prepared by Kneading

Hot press		Adhesion strength (kgf/cm ²)			Wood failure (%)
Temp (°C)	Time (min)	Av.	Max	Min	
130	15	57	85	40	13
	20	120	133	94	38
	25	136	156	124	92
100	25	62	82	50	13
	30	124	137	107	77
80	35	73	97	51	36
	40	101	126	73	40

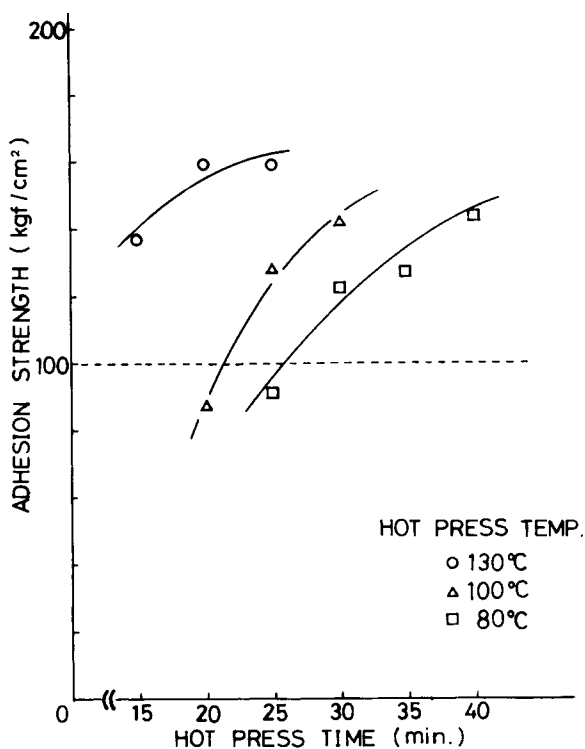


Fig. 4. Dry bond strength of CM wood-resorcinol adhesive prepared by the kneading method. CM wood was prepared by using the standard amount of etherifying agent; CM wood:resorcinol = 1:1 (wt); hot-press temperature: (□) 80°C; (△) 100°C; (○) 130°C.

From the figure, it is known that when the hot-press temperature is maintained at 130°C, the glue line temperature can exceed 80°C after 5 min. Generally, resorcinol resin adhesive is recognized as a medium temperature curing adhesive, and can be cured 3-dimensionally at 80°C within 10 min. Therefore, it can be said that, unlike the above-mentioned CM wood-phenol resin adhesive, chemical thermosetting is possible for this CM wood-resorcinol resin adhesive after hot-pressing at 130°C for 15 min. This is confirmed by the difference in the waterproof adhesion strength between these two adhesives. That is, when glued at 130°C for 20 min, the adhered specimens with either type of the adhesives showed sufficient adhesion strength as far as the dry bond strength is concerned. However, when the same specimens were subjected to a "boil-dry-boil" cycle test to evaluate the wet adhesive strength, delamination, and complete dissolution of glue line adhesive occurred during the first 4 h of boil in the case of the CM wood-phenol resin adhesive, whereas delamination did not occur even after the second boil in the case of CM wood-resorcinol resin adhesive. In the latter case, the average wet bond strength was measured to be 3.68 kgf/cm², the value considerably less than that of JIS specification. This unsatisfactory waterproof glueness can, partly, be attributed to the water solubility of carboxymethyl cellulose, a main component of the adhesive. Thus, addition

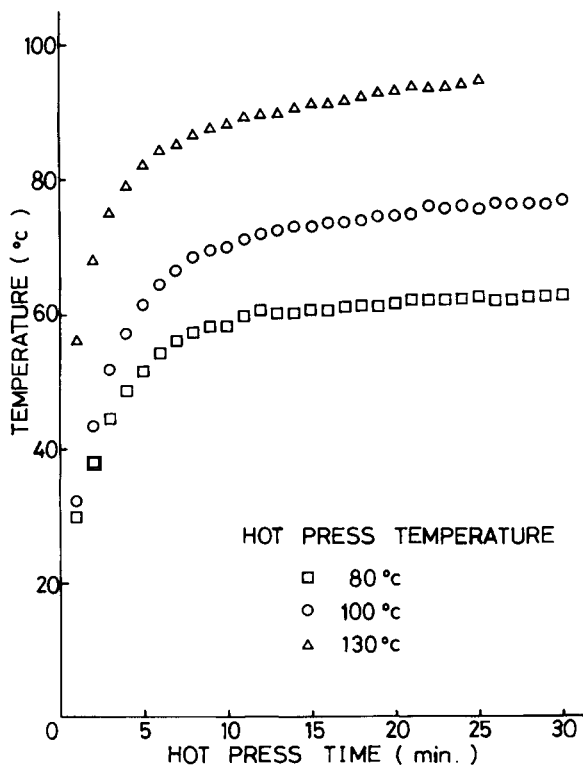


Fig. 5. Change in glue-line temperature with hot-press time. Thickness of adherend = 10 mm; hot-press temperature: (□) 80°C; (○) 100°C; (△) 130°C.

of crosslinking agent for cellulose can effectively enhance the waterproof gluability as shown in a later section.

It can be concluded here that adhesives prepared basically by kneading CM wood with phenols followed by resinification after further addition of formaldehyde are promising. There are, however, some problems to be overcome. The one is their applicability: Application with spatula is always possible, but roller application causes difficulty. The other is that waterproof gluability is not satisfactory. There are also some problems in the adhesion test. The actual temperature at the glue line is not sufficient for the 3-dimensional curing of phenol resin adhesives. Therefore, attempts were made to solve these problems and to improve the adhesion strength. Another method of dissolving CM wood into phenols has been pursued in order to get final products with excellent applicability. That is, the dissolution of CM wood in phenols was attempted to enhance applicability by use of phenolysis catalysts.

Adhesive from CM wood by Phenolysis Dissolution Method

It has been known that when wood meal is reacted with phenols, (for example, phenol, *p*-cresol, *o*-phenol-sulfonic acid) in the presence of an acid catalyst, lignin-carbohydrate bonds and ether linkages in the lignin side

chain (especially benzyl ether bonds) are cleaved. This produces phenol derivatives of lignin, and causes dissolution of the wood meal into the reaction medium. In these cases, phenol is linked to lignin (especially at the α -position on the side chain of lignin) by carbon-carbon linkage at its ortho or para positions to the phenolic hydroxyl group (Fig. 6). In fact, it was shown that phenol-lignin obtained by phenolysis of wood meal under mild conditions (that is, treating with phenol containing 2% anhydrous hydrochloric acid at 60°C for 2-3 hrs) has chemical composition of $C_{42}H_{32}O_6(OCH_3)_5OH$ 3PhOH, revealing that 0.6 parts of the phenol is linked to one phenylpropane unit.⁶

Then, in the present experiment, the dissolution of CM wood into phenol by phenolysis was performed by treating it with phenol solution containing 14-18 wt % of hydrochloric acid based on phenol, at 80°C, as already described in a previous subsection. The process of dissolution, facilitated by the phenolysis, is shown in Figures 7-10. Dissolution of CM wood prepared by the standard method was attempted in equal amounts of phenol. At the first stage of dissolution, that is, just after CM wood was introduced into the flask containing a mixture of phenol and hydrochloric acid catalyst, only a part of CM wood meal was wetting by the phenol solution (Fig. 7). As the treatment proceeded for longer time, dissolution occurred gradually and finally the whole system changed its color to a black-brown paste. Figures 8 and 9 were taken after 15 and 30 min of treatment time, respectively. After allowing to stand for 30 min, followed by stirring for further 30 min, almost complete dissolution occurred (Fig. 10).

After the complete dissolution, the solution was neutralized and resinified in the presence of formaldehyde and sodium hydroxide catalyst as described in the experimental section. CM wood-phenol resin adhesives thus obtained were black brown liquids comparable to the commercial phenol resin adhesives (Fig. 11).

A typical adhesion property of this kind of adhesive is shown in Figure 12, which includes data comparable with those shown in Figure 2. That is, the compression shear adhesive strength of specimens glued at 130-150°C with the CM wood-phenol resin adhesives (CM wood:phenol = 1:1 wt) is shown as a function of hot-press time. When the adhesion strength of the

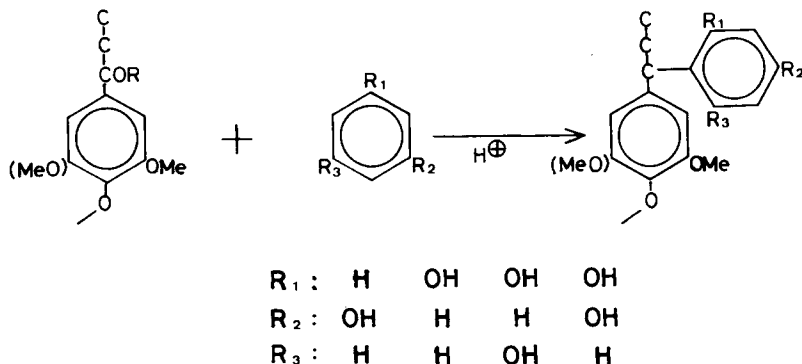


Fig. 6. Reaction of lignin with phenols.

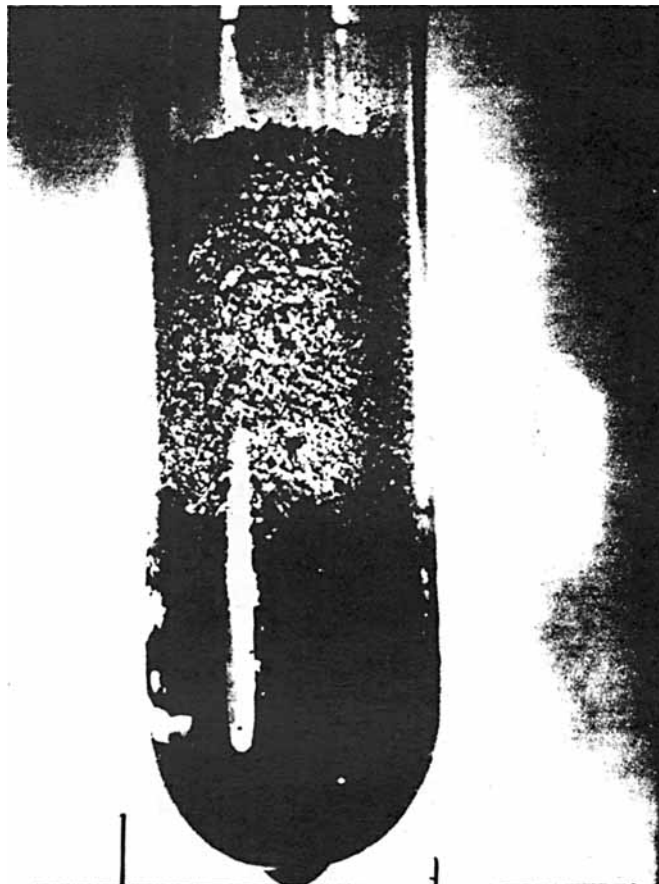


Fig. 7. Dissolution of CM wood into phenol facilitated by phenolysis. 5 min of dissolution; CM wood was prepared by using the standard amount of etherifying agent; CM wood:phenol = 1:1.

CM wood-phenol adhesives prepared by the kneading method (shown in Fig. 2) is compared to these resins, it can be pointed out that a longer hot-press time is necessary for these adhesives to attain the dry bond strength higher than JIS specification. This phenomenon can be explained in terms of the increase in the smaller molecular weight fractions in the adhesives by the phenolysis. Phenolysis in the presence of hydrochloric acid degrades wood components, yielding a significant amount of low molecular weight fractions. A longer hot-press time results in gradual polycondensation of this resol type adhesive. Thus, it can be said that CM wood-phenol resin adhesive prepared by the "phenolysis method" is a type of adhesive curable chiefly not by solvent-release mechanism but by a chemical thermosetting mechanism.

Therefore, it is required to use the adhesion conditions suitable for curing of resol type adhesives. In Figure 12, gluing was also attempted at 130, 140, and 150°C, but as can be known from Figure 2, the glue line temperature

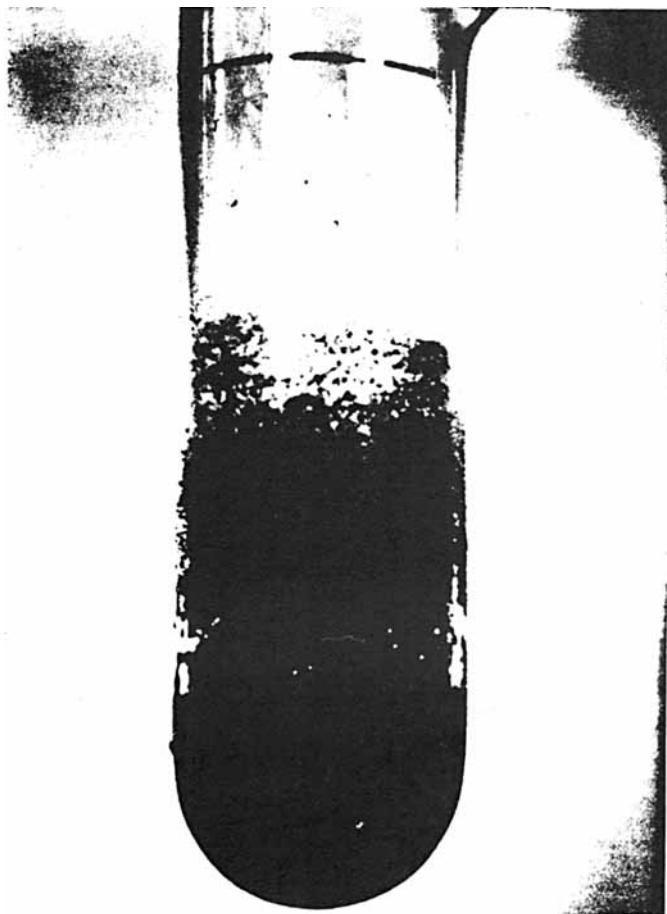


Fig. 8. Dissolution of CM wood into phenol facilitated by phenolysis (15 min of dissolution).

can not reach, even after 25 min, the temperature required for 3-dimensional curing of resol resin.

At any rate, it is imperative to raise the hot-press temperature until 3-dimensional curing of the adhesive layer occurs, in order to make good use of this CM wood-phenol resin adhesives. In this connection, suitable hot-press conditions were explored. The results of the examinations are shown in Figure 13. It can be seen from the figure, that a hot-press temperature of 170°C and a hot-press time of 20 min is necessary in order to realize the glue-line temperature of 130°C. These conditions of glueing are a bit severe and not practical, but, as the continuation of this study, this hot-press temperature was used in this experiment.

Figure 14 shows, as an example, that the dry-bond strength higher than JIS specification for phenol resin adhesives can be attained within 15 min of hot-pressing, when hot-press temperature of 170°C is used. Thus, at this hot-press temperature, the adhesion strength with respect to the hot-press time was found to be similar to that of Figure 2. That is, even though the

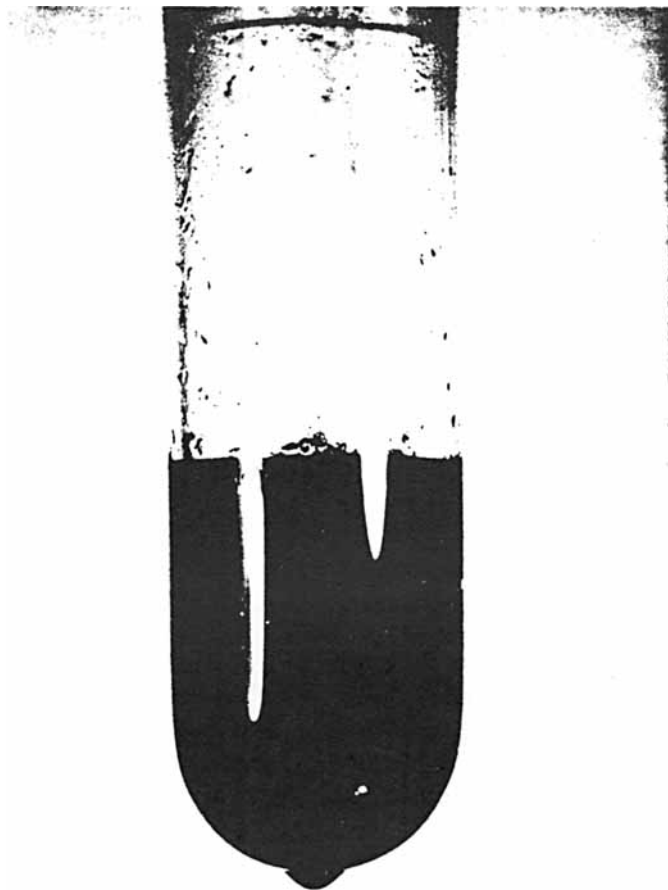


Fig. 9. Dissolution of CM wood into phenol facilitated by phenolysis (30 min of dissolution).

adhesive prepared by the phenolysis method includes a significant amount of low molecular weight fractions, the effect can be overcome by using a hot-press temperature of 170°C, which allows the 3-dimensional curing of adhesive layers.

The adhesive used in Figure 14 was not from the standard CM wood but from the one prepared by using one third amount of etherifying agents. As will be shown later, such adhesives obtained from a poorly substituted CM woods show higher waterproof adhesion strength. However, in this case, a larger amount of hydrochloric acid is required for the dissolution through phenolysis, compared with that of highly substituted CM wood. Therefore, the adhesives from poorly substituted CM wood include more highly degraded wood components, and are more difficult to provide satisfactory glueing criteria.

In that sense, results of the experiments on an adhesive from CM wood with a lower substitution are shown in Figure 14 rather than those obtained with adhesive from highly substituted standard CM wood. At any rate, an increase in hot-press temperature from 130 to 170°C improves the dry-bond strength to a great extent.

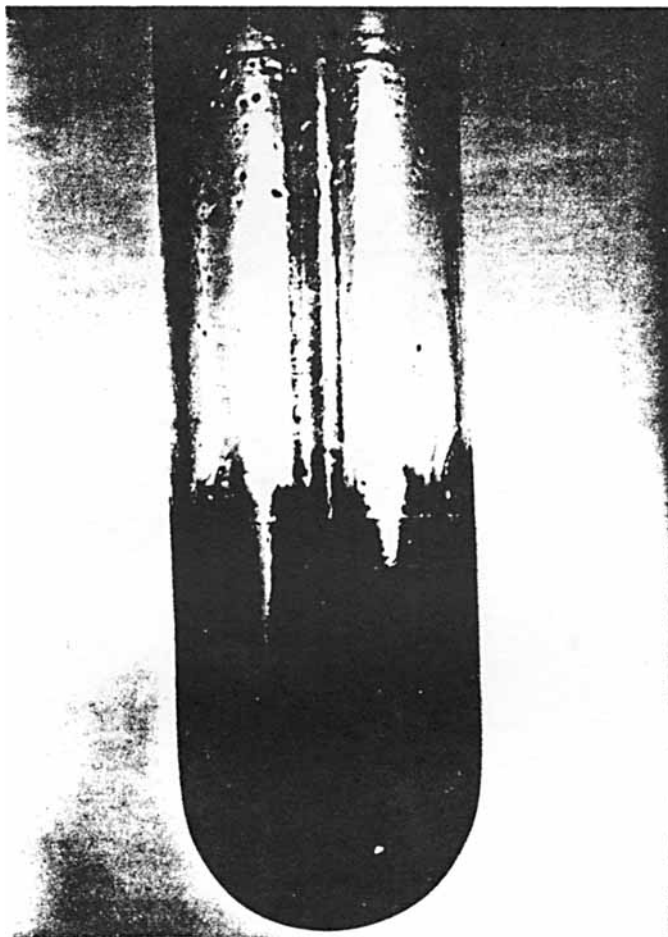


Fig. 10. Dissolution of CM wood into phenol facilitated by phenolysis (1 h of dissolution).

There is also some difference in waterproof adhesion strength between the specimens glued at the hot-press temperature of 130 and 170°C with the CM wood-phenol resin adhesive. However, the waterproof adhesion strength, even for the 170°C hot-press temperature, was found to be very poor. That is, when the specimen, glued with an adhesive from CM wood with a standard substitution at a hot-press temperature of 170°C for 25 min, were examined for their waterproof adhesion strength by a "boil-dry-boil" cycle test, delamination occurred during the first boil. This is probably because of the water soluble nature of carboxymethyl cellulose within CM wood. In that sense, the effect of the degree of substitution of CM wood on waterproof gluability was examined. By lowering the degree of substitution of CM wood, the degree of substitution of carboxymethyl cellulose in wood is correspondingly decreased and, hence, their solubility in water is also lowered. Actually, the decrease in CM substitution is found experimentally to be reflected in the increase in waterproof durability of CM wood-phenol resin adhesives. That is, specimens glued by the adhesives from CM woods etherified with one third and one fourth of the etherifying agent retained



Fig. 11. CM wood-phenol resin adhesive.

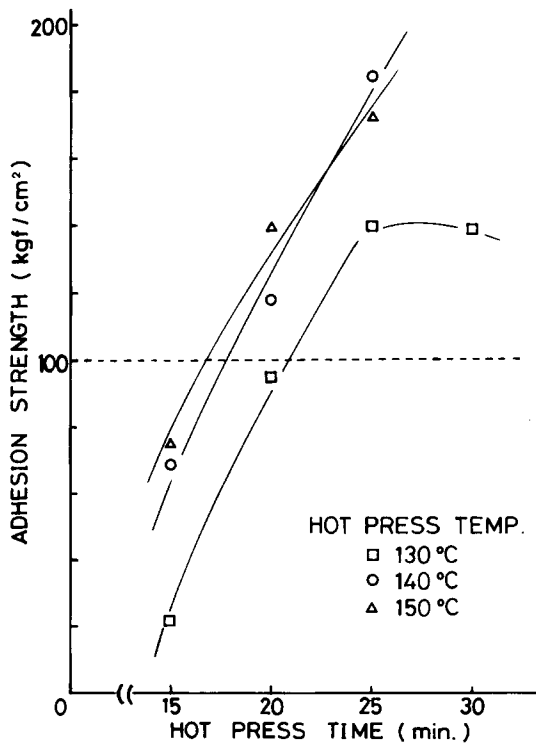


Fig. 12. Dry bond strength of CM wood-phenol resin adhesive prepared by the phenolysis method. CM wood was prepared by using the standard amount of etherifying agent; CM wood:phenol = 1:1 (wt); hot-press temperature: (□) 130°C; (○) 140°C; (△) 150°C.

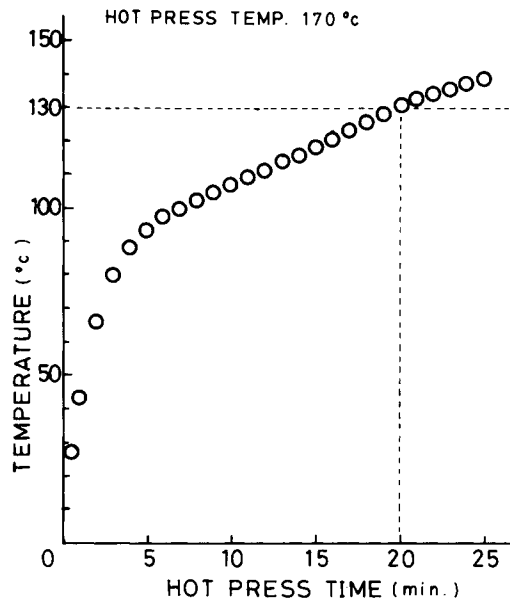


Fig. 13. Change in glue-line temperature with hot-press time. Thickness of adherend = 10 mm; hot-press temperature: 170°C.

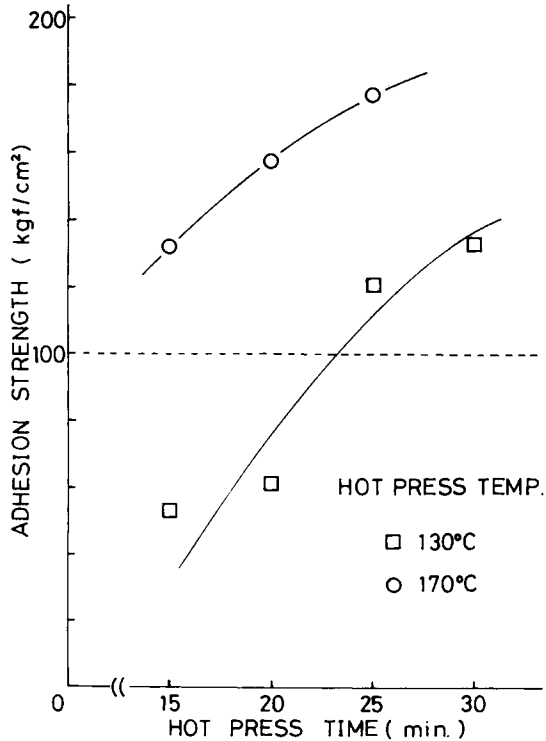


Fig. 14. Dry bond strength of CM wood-phenol resin adhesive prepared by the phenolysis method. CM wood was prepared by using one third of the standard amount of etherifying agents; CM wood:phenol = 1:1 (wt); hot-press temperature: (□) 130°C; (○) 170°C.

their glued state even after the second boil of the "boil-dry-boil" cycle test. The maximum wet-bond strengths after the "boil-dry-boil" test were 12.5 kgf/cm² and 17.8 kgf/cm² for the cases of the adhesives prepared with one third and one fourth of etherifying agents, respectively.

It is apparent from the above argument that a lowering of the degree of substitution of CM wood results in an increase of waterproof gluability of CM wood-phenol resin adhesives prepared from the CM wood, but the degree of waterproof gluability attained is not very satisfactory. Thus, attempts were made to improve the waterproof gluability of the CM wood-phenol resin adhesives.

The first trial was the use of a crosslinking agent for, especially, carboxymethyl cellulose. Polymeric MDI, a polyfunctional isocyanate compound, was used as the crosslinking agent. That is, three kinds of CM woods differing in the degree of substitution were dissolved in phenol by use of phenolysis, formalin was added, and the whole system was resinified. The polymeric MDI was added in 20 wt % quantity to the resol type CM wood-phenol resin adhesives. Press conditions were 170°C (hot-press temperature) and 25 min (hot-press time). The resulting specimens were examined by "boil-dry-boil" test, and the results are shown in Figure 15. In this figure, the compression shear adhesive strength of the specimens after the "boil-dry-boil" test, measured in wet state, is demonstrated as a function of the

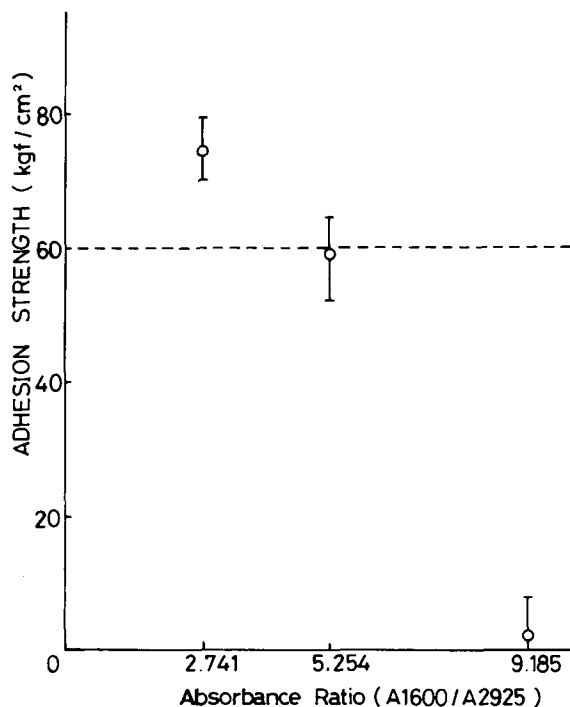


Fig. 15. Effect of the DS of CM wood on wet bond strength of CM wood-phenol resin prepared by the phenolysis method. 20% of the crosslinking agent (polymeric MDI) was added just before application. Three kinds of CM wood were prepared by using standard, one third and one fourth of the standard amounts of etherifying agents. CM wood:phenol = 1:1 (wt); hot-press temperature: 170°C.

degree of substitution of CM wood used as a component of each adhesive. The degree of substitution is shown as IR absorbance ratio (A_{1600}/A_{2925}). The CM wood prepared by the standard, one third, and one fourth amount of the etherifying agents corresponds to the absorbance ratio of 9.185, 5.254, and 2.741, respectively. From the figure, it is known that the effect of the addition of the crosslinking agent is significant and that the waterproof adhesion strength (that is, wet bond strength) becomes higher as the degree of carboxymethylation of CM wood, from which adhesive was made, becomes smaller. The adhesive prepared from CM wood with the lowest degree of etherification shows a wet-bond strength higher than the JIS specification for phenol resin adhesives, for a 20% polymeric MDI blend. This can be explained in two ways: (1) The hydroxyl group within CM wood increases with a decrease in the degree of etherification, resulting in a higher possibility of crosslinking reaction to occur; (2) a decrease in solubility of CM wood and carboxymethyl cellulose with the decrease in the degree of the etherification.

Judging from these results, it can be pointed out that the use of wood etherified to less extent can give adhesives with desired durability. However, in contrast, severe conditions of phenolysis are required as described in a previous subsection, when CM wood with a lower degree of substitution is dissolved. Hence, for further studies to enhance the waterproof gluability, CM wood prepared by using one third of the standard amount of etherifying agent was used. This CM wood has the balanced properties required to carry out phenolysis and to obtain waterproof gluability.

The second trial was to use an increased amount of formalin. There are possibilities of occurrence of the reaction between formaldehyde and the wood component. Formaldehyde can be reacted with "phenol lignin." Tollen's reaction and the Lederer-Manasse reaction are well known.⁷ It is logical to use a corresponding excess amount of formalin in addition to the amount used in a standard method of "resol" type adhesive preparation.

The molar ratio of formaldehyde to phenol, added during the preparation of the CM wood-phenol resin adhesive, was increased from 1.4 (which has been used as the standard amount) to 2.1. Other factors and conditions of the adhesive preparation were the same as used previously. Pressing was conducted, without adding the crosslinking agent, at 170°C for 25 min. After the "boil-dry-boil" test, the specimens show the average wet-bond strength of 48.4 kgf/cm² (the maximum strength: 59.4 kgf/cm², the minimum strength: 40.2 kgf/cm²). This value is slightly less than the JIS specification but is considered to be an almost satisfactory value. Then, it can be concluded, that increase in the formaldehyde amount results in a great improvement of the waterproof gluability of CM wood-phenol resin adhesives.

Furthermore, the combined effect of the increase in the formalin amount as well as the addition of a crosslinking agent was investigated. That is, the molar ratio of formaldehyde to phenol was increased from 1.4 to 2.1 and polymeric MDI, 20 wt % based on the amount of CM wood-phenol resin adhesive, was added and the whole system was used as adhesive. Waterproof gluability for these adhesives is shown in Figure 16. As shown in the figure, an increase in the amount of formaldehyde as well as the addition of crosslinking agent apparently increases the wet-bond strength,

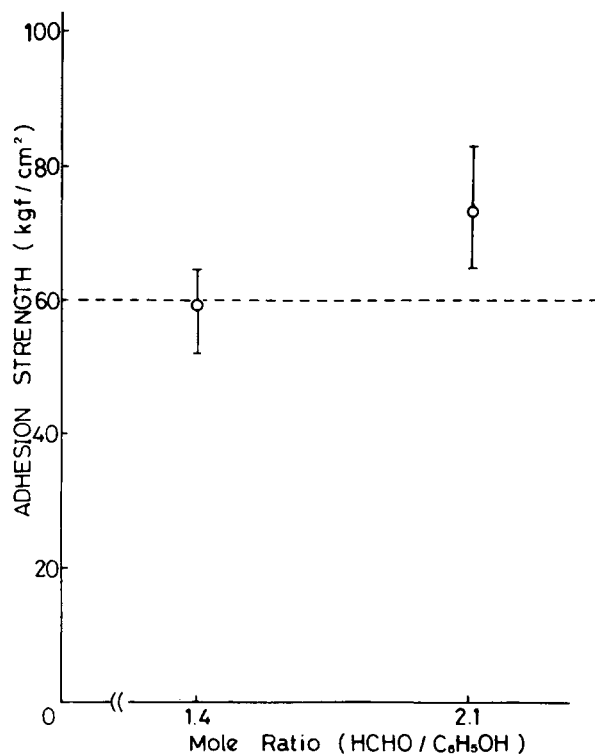


Fig. 16. Effect of the amount of formalin on wet bond strength of CM wood-phenol resin adhesive prepared by the phenolysis method. 20% of the crosslinking agent (polymeric MDI) was added just before application. CM wood was prepared by using one third of the standard amount of etherifying agent; CM wood:phenol = 1:1 (wt); hot-press temperature: 170°C.

and a waterproof adhesion strength higher than the JIS specification can be realized.

These results imply that the amount of formaldehyde in the CM wood-phenol resin adhesives, prepared by using the standard amount of formaldehyde, is insufficient to achieve 3-dimensional curing.

The third trial to enhance waterproof adhesion strength of CM wood-phenol adhesive is to replace 20% of phenol with resorcinol and to prepare CM wood-phenol-resorcinol resin adhesive. The weight ratio of CM wood:phenol:resorcinol was 5:4:1. The adhesives thus prepared were evaluated for their waterproof durability. After the "boil-dry-boil" test, the specimens showed average wet-bond strength of 80.3 kgf/cm² (maximum value: 87.7 kgf/cm², minimum value: 63.8 kgf/cm²). These values are quite satisfactory.

From these results, it can be concluded that a resol type adhesive, in which more than half of the phenol is replaced by the CM wood, can be prepared and that even the waterproof adhesion strengths of these CM wood-phenol resin adhesives could become excellent if suitable preparation conditions are adopted. However, the present study has only been aimed at to find out the possibility of preparing adhesives from CM wood. Adhesion strength of CM wood-phenol adhesives might be enhanced by adding some

suitable additives, such as fillers, reaction accelerators, and their application could also be improved by adding water, surfactants, etc. By using veneers as adherends, low hot-press temperature, as in the case of commercial wood adhesives, can be used. And, what is more important, is that the data would be comparable to already published data on conventional commercial adhesives.

Further experiments, considering these aspects, are in progress now, and will be reported in the near future.

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Received September 18, 1985

Accepted January 24, 1986