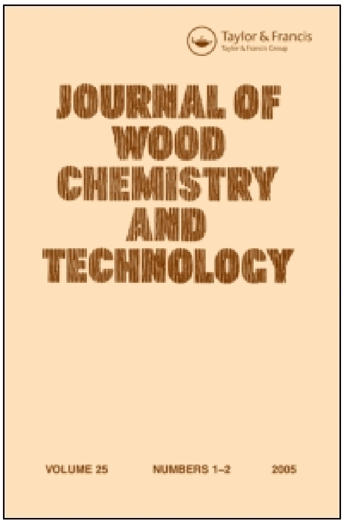

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N. Shiraishi[a]; H. Itoh[a]; S. V. Lonikar[a]; N. Tsujimoto[b]
[a] Department of Wood Science and Technology, Kyoto University, Kyoto, Japan [b] Central Research Laboratory, Oji Paper Company, Ltd., Tokyo, Japan

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ADHESIVES PREPARED FROM HYDROXYETHYLATED WOOD WITH OR WITHOUT EXPLOSION PRETREATMENT

N. Shiraishi, H. Itoh and S. V. Lonikar

Department of Wood Science and Technology, Kyoto University
Sakyo-ku, Kyoto 606, Japan

N. Tsujimoto

Central Research Laboratory, Oji Paper Company, Ltd.,
Shinonome, Koto-ku, Tokyo 135, Japan

ABSTRACT

Preparation of hydroxyethylated wood-phenol resin adhesives has been attempted. The steam-explosion pretreatment or the phenolysis of the chemically modified wood was found to enhance its solubility making it feasible to prepare adhesives with good properties and workability. Thus, water soluble hydroxyethylated wood-phenol resin adhesives, comparable in gluability with the commercial resol type phenol resin adhesives could be obtained. The JIS specification for the dry adhesive strength was easily surpassed in case of these adhesives. By setting the glue line temperature at 130-150°C, which is necessary for three-dimensional curing of resol adhesive, and using other suitable gluing conditons, water-proof adhesion was also attainable. The water-proof adhesion could be enhanced by the addition of crosslinking agent (polymeric MDI) into the hydroxyethylated wood-phenol resin adhesives, resulting in fulfilment of the JIS specification for both the dry and water proof adhesive bond strength.

INTRODUCTION

In a previous paper, it was shown that the thermoplastic properties of acylated wood can be enhanced by the steam-explosion treatment of wood prior to the acylation[1]. On the other hand, it was found that the chemical modifications such as esterification or etherification can render the wood soluble in neutral organic solvents or aqueous solvents depending upon the type of chemical modification, besides conferring significant thermoplastic properties[2-7]. In continuation with these findings, attempts were made to enhance the solubility of hydroxyethylated wood, one of the representative chemically modified woods, by steam-explosion treatment prior to the etherification. And then, conversion of hydroxyethylated woods prepared with or without the steam-explosion pretreatment, into reactive solution-type adhesives and their gluability have been studied and described in the present paper. That is, in the present case, the chemically modified woods were used to synthesize phenol-formaldehyde type adhesives, in which, hydroxyethylated woods were, first, tried to dissolve in phenol and then used as a main component of the phenol resin adhesives.

In the past, several reports have appeared on the use of lignin as a main component in preparing adhesives while the use of whole wood in making adhesives is seldom reported, except those of ours[2-4].

EXPERIMENTAL

1. Materials

Makanba (birch : Betula maximowiczii Regel) and Shirakaba (white birch : Betula platyphylla Japonica) wood meals (cold water extracted, 20-80 mesh) as well as steam-exploded wood meal from Shirakanba were used for hydroxyethylation. All the chemicals used were of "extra-pure" grade or "guaranteed reagent" grade and were used without further purification.

2. Steam-explosion Pretreatment of Wood Samples

Shirakanba wood meal was subjected to steam-explosion pretreatment in the same way as described in the previous paper[1]. The pre-explosion steaming temperature used was 170-210°C. The steam-exploded wood meals were then freeze-dried. Among these steam-explosion pretreated wood meals, samples with pre-explosion steaming treatment of 170°C for 2 min and 210°C for 15 min were mainly used in the present investigation and are designated as Ex(1)-W and Ex(2)-W, respectively.

3. Hydroxyethylation

Hydroxyethylation of wood was carried out in accordance with the conventional method using isopropanol as the solvent[8)] but with a slight modification. That is, in the case of unexploded wood meal (Makanba and Shirakanba) and wood meal (Shirakanba) steam-exploded under mild conditions (170°C/2 min), the hydroxyethylation was achieved as follows : Wood meal sample (60 g) was suspended in 750 ml of isopropanol and then 16 % aqueous sodium hydroxide solution containing 18 g of the solute was added dropwise over a period of 10 min under continuous stirring. The stirring was continued throughout the reaction. After 1 hr stirring at the room temperature, 60 g of ethylene oxide was added at once and the reaction vessel was tightly closed. Then the temperature was raised to 55–60°C over a period of 1 hr and the reaction was allowed to proceed for 5 hr in this temperature range. At the end of the reaction period the supernatant liquid was decanted off and the reaction product was washed three to four times with methanol-acetone mixture (1:1 by volume). Then, the product was collected by filtration through G-2 sintered funnel, dried in an air-circulated oven at 70°C overnight, vacuum dried at 70°C for 24 hr, weighed and the weight increase (W.I.) of the sample was calculated. Both the hydroxyethylated wood meals from the untreated wood and the steam-exploded wood meal under mild conditions (Ex(1)-W) have the same apparent weight increase of 28 % after the etherification.

On the other hand, because of the high solubility of the wood meal steam-exploded under severe conditions, such as pre-explosion steaming at 210°C for 15 min, in the hydroxyethylation medium, the hydroxyethylated wood, in this case, was recovered by distilling off all the volatile parts of the reaction medium by using a rotary evaporator at temperatures up to 100°C after completion of the reaction and neutralization with acetic acid. The product was further dried by freeze-drying and used for subsequent experiments without further purification. The extent of reaction, in this case, can not be evaluated from the value of weight increase. However, it is suggested from the comparison of the IR absorption bands for Ex(2)-H.E.W. and Ex(1)-H.E.W. that the degree of substitution in both cases is almost the same.

4. Preparation of Phenol-Hydroxyethylated Wood Adhesives

4.1. Direct Method

Steam-exploded-hydroxyethylated wood exhibits excellent solubility and thus an adhesive can be prepared by dissolving the etherified wood into phenol and resinifying directly by conventional method[9]. That is, 5 g of steam-exploded-hydroxyethylated wood and 5 g of phenol were weighed into a 50 ml two necked flask, 10 ml of water was added, and the contents were stirred at 80-90°C for 30 min to obtain a clear solution. Then, 40 % aqueous sodium hydroxide solution containing 0.1 g of the alkali was added and stirred further for 10 min at the same temperature. Formalin, 6.5 g, was added at this stage, thereby, methylolation and the partial condensation were proceeded under constant agitation at 80-90°C for 3 hr to result in a precondensation product of phenolic resin. To the prepolymer (resin solution) 40 % aqueous sodium hydroxide containing 1 g of alkali was added and stirred for several minutes to obtain a paste-like adhesive.

In addition, in the case of wood steam-exploded under severe conditions and hydroxyethylated (Ex(2)-H.E.W.), the mixing ratio of etherified wood to phenol was increased to 7:3 and 9:1 in order to obtain phenol resin adhesives containing a large amount of wood component.

On the other hand, in the case of wood hydroxyethylated without steam-explosion pretreatment (H.E.W.), the etherified wood

(5 g) was mixed with 25 g of water in a kneader (Irie Shokai, PBU-0.1 type) at room temperature for 3 hr and the paste obtained was transferred to a two necked flask and resinified by using phenol, formalin and aqueous sodium hydroxide as described above.

4.2. Phenolysis Method (Dissolution of Hydroxyethylated Wood Facilitated by Phenolysis)

As the hydroxyethylated wood prepared by etherification without steam-explosion pretreatment was found to dissolve well into phenol under the conditions which lead to phenolysis of lignin in wood, hydroxyethylated wood-phenol resin adhesives were prepared by aiding the dissolution process by phenolysis. That is, 5 g of phenol was weighed into a 50 ml two necked flask and melted at 50°C. Hydrochloric acid (2-10 wt% based on the amount of phenol) was added to the flask as 35% aqueous solution and the contents were mixed well. To the above solution, 5 g of hydroxyethylated wood meal was added. The flask was closed and allowed to stand at 80°C for 1 hr, followed by stirring at the same temperature for 30 min to obtain a clear solution. The contents were then neutralized by dropwise addition of 40% aqueous sodium hydroxide solution. The subsequent resinification and adhesive preparation were carried out in line with the procedure described in the above section. The appearance of the product ranged from aqueous solution to aqueous paste, depending upon the amount of hydrochloric acid added at the stage of phenolysis.

As a comparison, a commercial phenol resin adhesive (Oshika Shinko Ltd. Deernol No. 17) was used as described later.

5. Improvement of Water-Resistance of Adhesives by Crosslinking

Polymeric MDI (4,4'-diphenylmethane diisocyanate ; Oshika Shinko Co. Ltd. H-3 M) was used as a crosslinking agent. The crosslinking agent, 20 parts, was added to 100 parts of chemically modified wood-phenol resin adhesives and blended well just before use to improve water resistance of the adhesives.

6. Adhesion Test

Wood specimens (Makanba edge grain cut) of 30(L)x25(R)x10(T) mm size were glued together with grain directions parallel, using 25(L)x25(R) mm surface as gluing area to get samples for the compressive shear adhesive strength test. Amount of adhesive used was ranged from 320 to 370 g/m^2. After the application of the adhesives, the overlapped adhesion specimens were cold-pressed for 20 min. Curing was achieved by hot pressing the test specimens under 10 $kgf.cm^{-2}$ pressure (1 $kgf.cm^{-2}$ = 0.0981 MPa = 14.22 psi) at definite temperatures for definite periods, followed by cold pressing at room temperature under the same pressure. Shear adhesive strength tests were performed by compression loading according to the Japan Industrial Standard (JIS) K-6852 for phenol resin adhesives, to evaluate dry bond strength. In this case, the loading speed is 2 mm/min and sample conditions is air dried. On the other hand, in order to evaluate water-proof adhesion, glued specimens were subjected to "boil-dry-boil" cycle test. That is, the test specimens were placed in boiling water for 4 hr, dried in an air-circulated oven at 60°C for 20 hr, again kept in boiling water for 4 hr, cooled by immersing in cold water (20°C) and tested in wet state for shear adhesive strength as mentioned above.

7. 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 glue line and the temperature change was recorded throughout the pressing time using a multichannel digital recorder (Takada Riken Ltd.).

RESULTS AND DISCUSSION

Preparation of Adhesives by 'Direct Dissolution' Method and Their Gluability

1. Hydroxyethylated Wood-Phenol Resin Adhesives

Water soluble hydroxyethylated wood-phenol resin adhesives were prepared from hydroxyethylated woods prepared after steam-explosion pretreatment (Ex(1)-H.E.W., Ex(2)-H.E.W.) by using the procedure described in the experimental section (4.1.). These adhesives containing 35-40% resin content were finally used and tested for adhesive strength. On the other hand, hydroxyethylated wood prepared without steam-explosion pretreatment (H.E.W.) did not give a homogeneous solution by the same procedure, that is, mere stirring. In this case, a considerable amount of wood powder remained in solution. So, complete dissolution was pursued by mixing the etherified wood first with water in a kneader. Then, phenol, sodium hydroxide and formalin were added and reacted in accordance with the conventional method 9) to obtain aqueous phenol resin adhesives as described also in the section 4.1. This adhesive was used after adjusting the final viscosity to that of a commercial phenol resin adhesive (Oshika Shinko Ltd. Deernol No. 17), by diluting with water. Usually, the resin content of the adhesive used for test specimens was around 45%.

2) Adhesion with Hydroxyethylated Wood-Phenol Resin Adhesive

Results of the adhesive bond strength tests of the specimens glued by using the adhesives mentioned above at pressing temperature of 140°C under 10 $\mathrm{kgf.cm^{-2}}$ pressure for different pressing time are shown in Table 1. The wood failure values are average values and the variability of the values became greater with a decrease in the value. Dependence of the average adhesive strength on pressing time is graphically shown in Fig. 1. Each of the value recorded in Table 1 is an average of five trials. It was found that pressing time of less than 15 min also gave a higher shear adhesive strength than JIS specification (100 $\mathrm{kgf/cm^2}$), for adhesives prepared from the wood hydroxyethylated without steam-explosion pretreatment or with mild steam-explosion pretreatment, and that the latter, which shows higher solubility compared to the former, reveals better adhesion results. In this

TABLE 1

Compression shear adhesive strength and average wood failure (Number of test specimens : 5)

Sample	Hot Press Time (min)	Dry Adhesive Strength (kgf/cm^2) Ave.	Max.	Min.	Wood Failure (Ave.) (%)
H.E.W.	15	140	168	124	2
	20	160	181	123	12
	25	160	187	132	37
	40	219	264	151	70
Ex(1)-H.E.W.	15	209	251	123	67
	20	176	200	138	63
	25	199	210	178	95
	40	231	246	206	100
Ex(2)-H.E.W.	15	62	71	30	0
	20	92	121	68	17
	25	124	152	118	22
	40	171	200	147	57

connection, a commercial phenol resin adhesive (Oshika Shinko Ltd. Deernol No. 17) was used, in its standard composition, to adhere the test specimens under the same gluing conditions. The results show an average shear adhesive strength of 202.4 kgf/cm^2 and wood failure of 30% for 15 min pressing time, and an adhesive strength of 208.0 kgf/cm^2 and wood failure of 58% for 20 min pressing time. These findings indicate that replacement of half of the phenol with hydroxyethylated wood does not decrease the gluability as far as dry adhesive strength was concerned.

On the other hand, in the case of hydroxyethylated wood-phenol resin adhesives prepared from steam-exploded wood under severe conditions (Ex(2)-H.E.W-phenol resin adhesive), adhesive strengths are not very high as a whole, and 25 min of hot pressing is needed to meet the above mentioned JIS specification. As factors for this phenomenon, it can be pointed out that

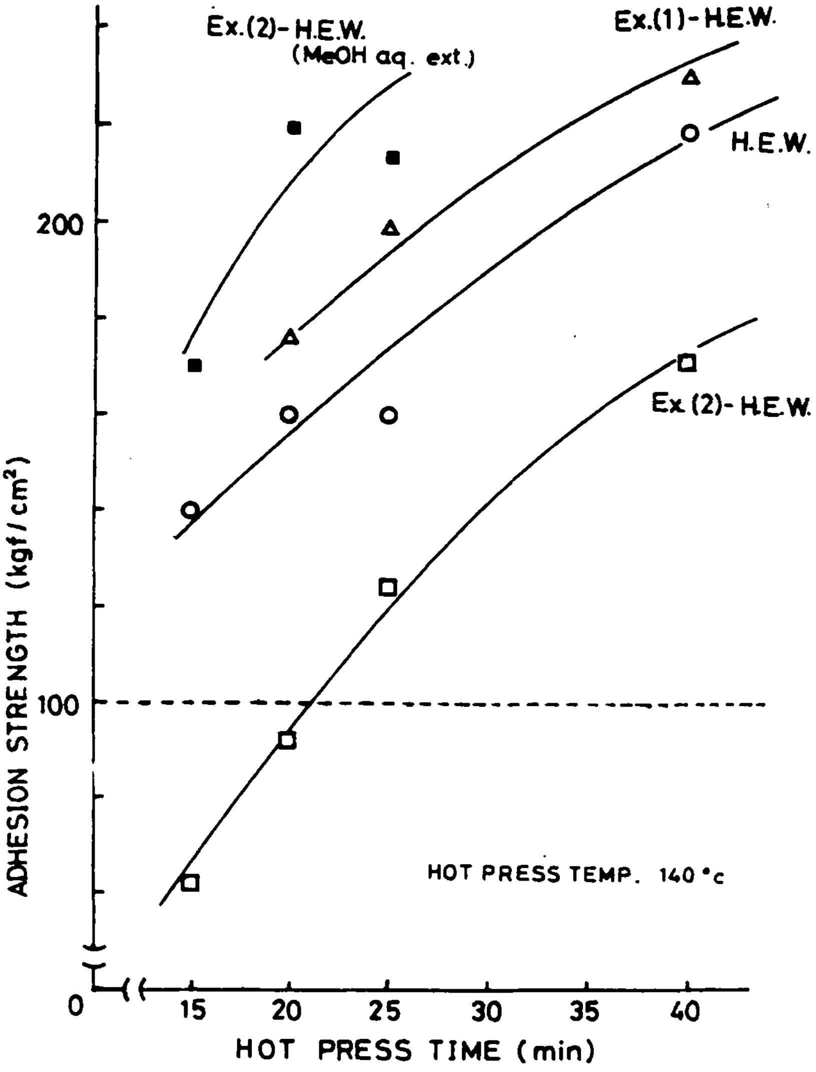

FIGURE 1 Compression shear adhesive strength (dry adhesive bond strength) of wood specimens glued with hydroxyethylated wood-phenol resinified adhesives.

o : H.E.W.-Phenol resin ; ▲ : Ex(1)-H.E.W.-phenol resin ; ▢ : Ex(2)-H.E.W.-phenol resin ; ■ aqueous methanol extracted Ex(2)-H.E.W.-phenol resin.

depolymerization of wood components proceeds to a significant extent[10, 11], and contamination with low molecualar weight compounds such as salts yielded by neutralization gives adverse effects. Then, these low molecular weight compounds were tried to extract by 70% aqueous methanol, followed by phenol resinification. The results of the adhesion test on the purified hydroxyethylated wood-phenol resin adhesive are also shown in Fig 1, revealing the highest adhesiveness, in accordance with the above statement.

On the other hand, water-proof gluability was examined as mentioned in the experimental section for these three adhesives. The test specimens were found to be delaminated during the first boiling procedure, even those glued at 140°C for 40 min. For comparison, the water-proof adhesion was examined for the specimens glued with the above mentioned commercial phenol resin adhesive. The results obtained are similar : delamination occured during the first boiling cycle. The poor water-proof adhesion may be explained as follows. The thickness of the test specimen is thick, that is, 1cm, which makes the rather big distance between the upper and lower hot plate (2cm), and so heat transferred to glue line is insufficient for curing of the adhesives.

The adhesives used are resol type adhesives and require high temperature (130-150°) for the achievement of complete, three dimensional curing. To obtain quantitative information concerning this point, the actual glue line temperature was measured and the results are shown in Fig. 2. From the Figure, it becomes clear that the glue line temperature can not reach to 100°C even after 25 min of pressing time, when the hot press temperature is maintained at 140°C. Obviously, this glue line temperature is far less than the temperature required for the three dimensional curing of the resol type adhesives. Accordingly, it can be concluded that the above results of adhesion using hydroxyethylated wood-phenol resin adhesives were mainly obtained by solvent-release during adhesion.

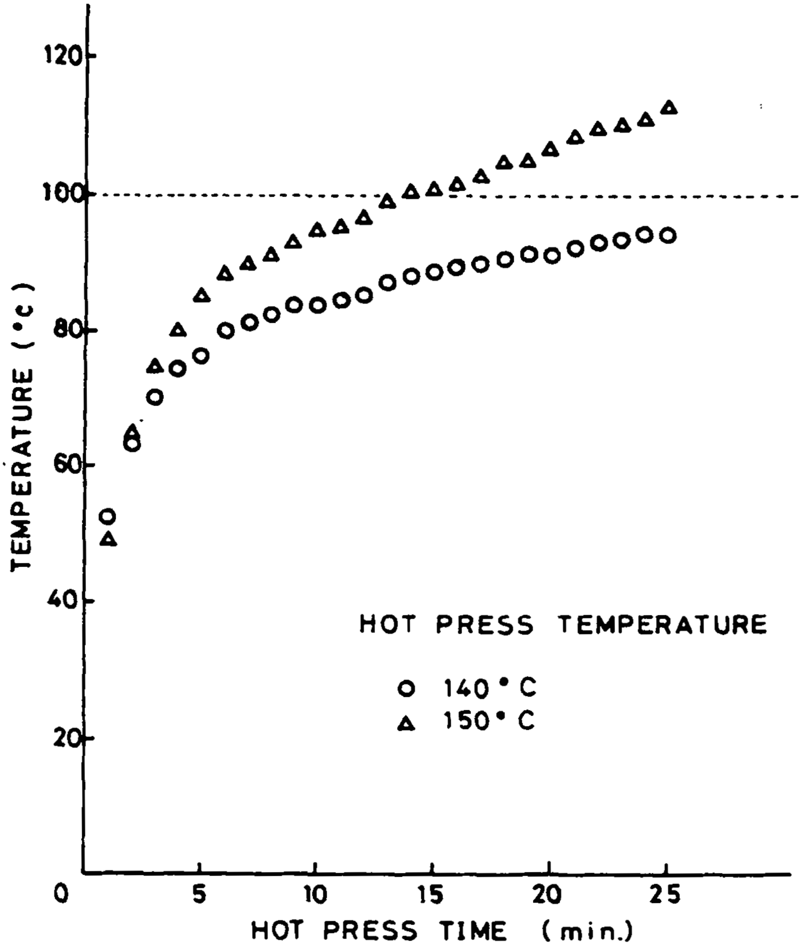

FIGURE 2 Relation between actual glue line temperature and hot press time. Thickness of wood adherend : 1 cm ; hot-plate temperature : 140°C and 150°C

In this case, it is logical that the adhesive which contained large parts of low molecular weight fraction, such as the adhesive prepared from wood steam-exploded under severe conditions, can not give high and excellent adhesion, and gives poor water-proof gluability. The role of the solvent release type adhesion can be deduced from the following experiment in which the content of hydroxyethylated wood in adhesive was increased and their bonding properties were examined. That is, hydroxyethylated wood-phenol resin adhesives were prepared, using hydroxyethylated wood etherified after severe steam-explosion pretreatment (Ex(2)-H.E.W.) and changing the ratio of Ex(2)-H.E.W. to phenol from 5:5 to 7:3 and 9:1. The results of shear tests of adhesive bond by compression loading on specimens, adhered with these adhesives at 140°C under 10 $kgf.cm^{-2}$ pressure are shown in Fig. 3. From the Figure, it can be found that even though the wood content increases the bonding strength increases rather than decreases. This result shows the contribution of cohesive strength of high molecular weight fractions among wood components to the adhesive strength and can be understood in light of the above mentioned solvent release mechanism.

As the extension of this experiment, adhesive trials using higher hot-press temperature should be done so as to allow complete, three-dimensional curing. This is discussed in detail in later sections.

Preparation of Hydroxyethylated Wood-Phenol Adhesives by use of 'Phenolysis Dissolution' Method and Their Gluability

Among the adhesives hitherto mentioned, the adhesives prepared from unexploded wood had some problem during dissolution which did not give a clear solution, so that the workability during adhesive application to adherends was not satisfactory. Moreover, it was necessary to use a kneader during its preparation.

In order to overcome this problem the dissolution of hydroxyethylated wood in phenol was tried to enhance by use of

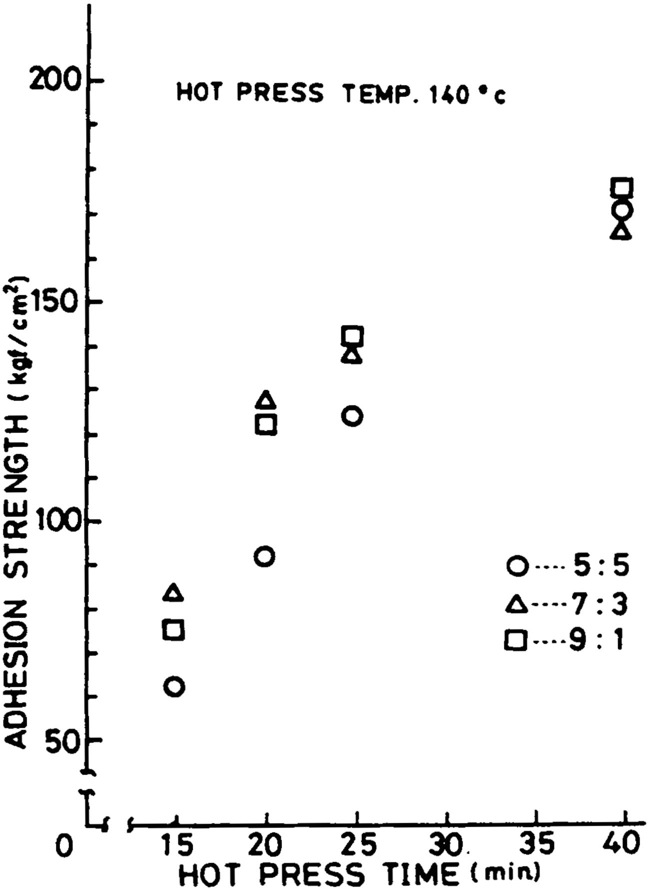

FIGURE 3 Compression shear adhesive strength (dry adhesive bond strength) of wood specimens glued with Ex(2)-H.E.W.-Phenol resinified adhesives with different wood composition. Ex(2)-H.E.W. : phenol (by weight) = 5:5 (o) ; 7:3 (△) ; 9:1 (□)

phenolysis catalysts. By this phenolysis treatment, intramolecular bonds of lignin are partly broken and at the same time, a certain amount of phenol is introduced into lignin molecule, especially, at α-position on the side chain. Both reactions can enhance the solubility of hydroxyethylated wood into phenol. The adhesive thus obtained had clear appearance and better workability. It is actually known that when wood meal or lignin is heated in phenol in the presence of acid catalysts, the ether linkages in the lignin side chain, especially benzyl ether bonds are cleaved, producing a phenol derivative of lignin12) and causing dissolution into the reaction medium. Depending on the reaction conditions, phenolysis of lignin side chains would be followed by the phenol exchange reactions occuring for non-condensed nuclei of lignins. In these cases, phenol is linked to lignin by carbon-carbon linkage at its ortho or para positions to phenolic hydroxyl group. In fact, it was shown that12) 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 hr) 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. Then, in the present experiment, the dissolution of hydroxyethylated wood into phenol by phenolysis was performed by treating it with phenol solution containing 2-10 wt% of hydrochloric acid based on phenol, at 80°C. The ratio of hydroxyethylated wood to phenol was either equiamount or excess of the etherified wood. At the early stage of the dissolution process, the hydroxyethylated wood meal was only partially impregnated with the phenol solution. However, when this mixture was allowed to stand for about 1 hr, it changed to a brown (black) paste. By stirring this paste continuously for 30 min, almost complete dissolution occured giving the desired solution. At this stage, the solution was neutralized, a definite amount of formalin was added and resinified using sodium hydroxide as a catalyst as described in the experimental section.

TABLE 2

Compression share adhesive strength and Wood failure of wood specimens glued with H.E.W.-phenol resinified adhesives prepared by use of phenolysis during its dissolution process.
Hot-press temperature : 140°C
(Number of test speciments : 5)

Sample	Hot Press Time (min)	Dry Adhesive Strength (kgf/cm^2)			Wood Failure (Ave.) (%)
		Ave.	Max.	Min.	
HCl 2wt.%	15	156	178	136	22
	20	160	194	127	43
	25	165	194	131	53
HCl 4wt.%	15	146	166	126	5
	20	146	166	126	8
	25	181	200	130	68
HCl 10wt.%	15	64	103	18	2
	20	73	85	69	0
	25	127	165	94	25
	40	179	234	126	89

The appearance of the adhesive finally obtained depends upon many factors, including the amount of hydrochloric acid added. When hydrochloric acid was added in more than 4 wt% based on the amount of phenol, homogeneous solution type adhesive was obtained. When the amount of hydrochloric acid was less than 3 wt% based on the phenol, the adhesives finally obtained were paste-like liquid containing a small part of undissolved wood meal.

The shear-test of adhesive-bond by compression loading with specimens glued with these adhesives at press temperature of 140°C are shown in Table 2. From the Table, the adhesive prepared after dissolution in the presence of 4 wt% hydrochloric acid is found to be prospective for workability and gluability. As the amount of hydrochloric acid added becomes excess, for example, 10 wt% based on phenol, the gluability becomes poor. It is understandable that

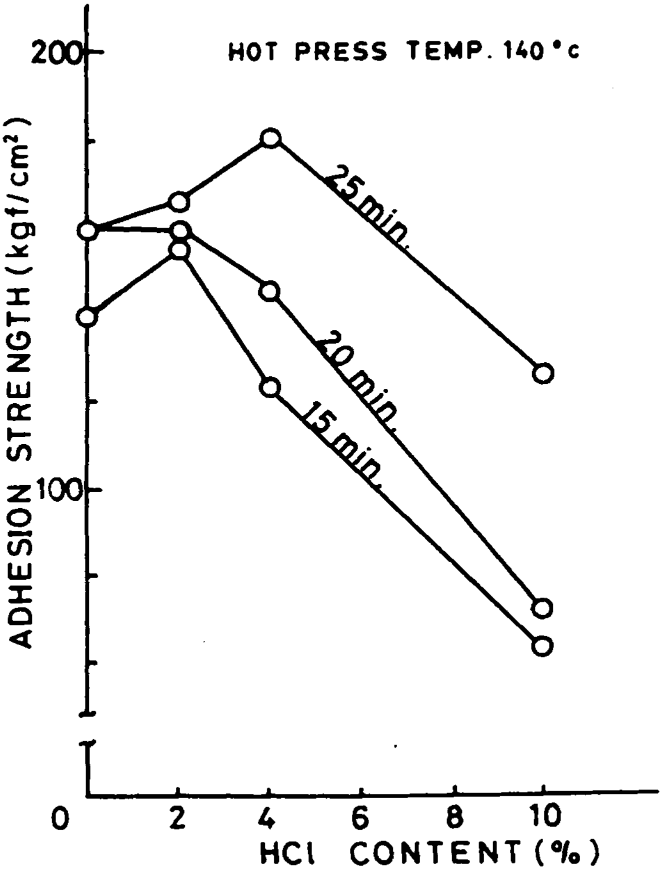

FIGURE 4 Dependence of the adhesive strength, for different pressing time, on the amount of hydrochloric acid (wt%, based on phenol) which was used as a phenolysis catalyst during the preparation of hydroxyethylated wood (H.E.W.)- phenol resinified adhesive.

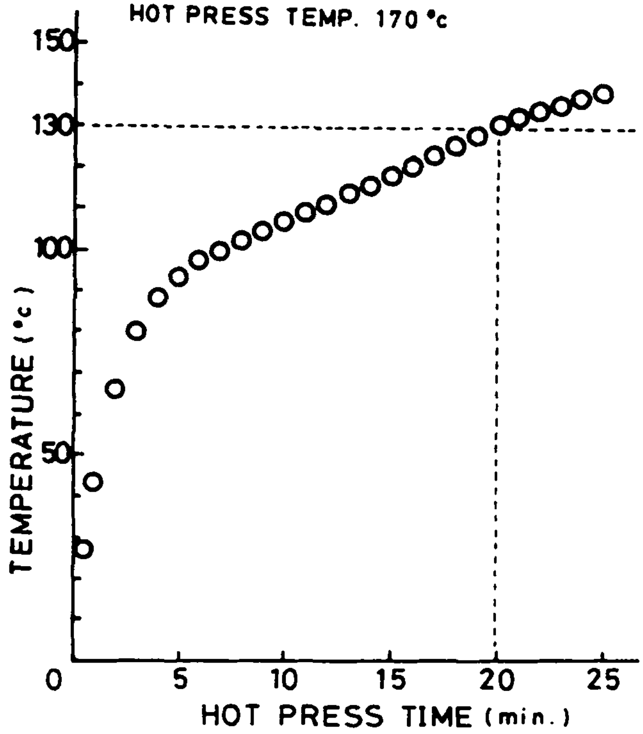

FIGURE 5 Relation between actual glue line temperature and hot press time. Thickness of wood specimen : 1 cm ; Hot-press temperature : 170°C

this is caused by the excessive depolymerization of main wood components. This trend can be clearly recognized from Fig. 4 in which dependence of bond strength on the concentration of hydrochloric acid added, is examined with pressing time as a parameter.

When the water-proof gluability was examined for these glued specimens by 'boil-dry-boil' cycle test, the same results were obtained as described previously that is, all the specimens were delaminated during first boiling process. This is also thought to be caused from the lower temperature applied to the glue line than necessary for three dimensional curing of adhesive layer. Then,

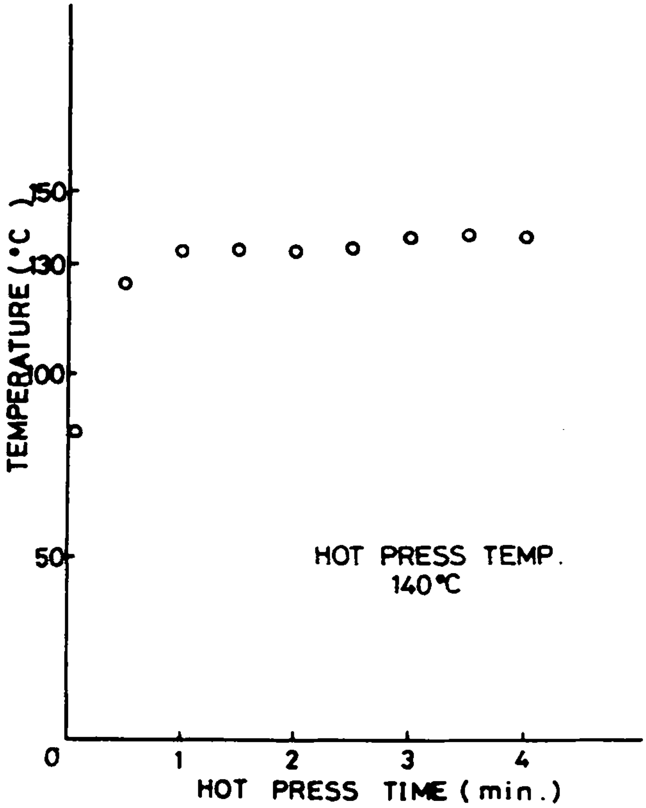

FIGURE 6 Relation between actual glue line temperature and hot press time. Thickness of wood specimen : 1 mm ; Hot-press temperature : 140°C

it was investigated to find out a press temperature necessary to cause complete curing of the resol type resin. A meaningful result is shown in Fig. 5. From the Figure, it is clear that glue line temperature of 130°C can be attained after 20 min of hot pressing, when the hot-press temperature was set at 170°C. In this connection, the glue line temperature change was also measured in the case of gluing three sheets of thin Makanba veneers (1 mm thick). The results are shown in Fig. 6, showing

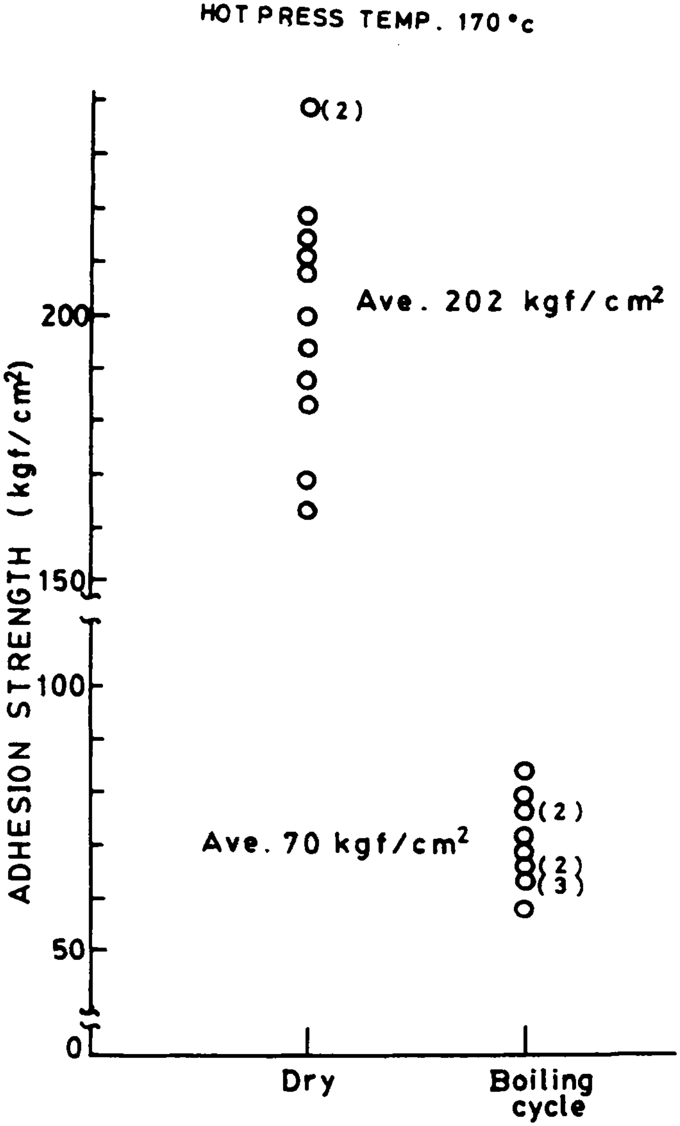

FIGURE 7 Dry and water-proof compression shear adhesive strengths of wood specimens glued with hydroxyethylated wood (H.E.W.)-phenol resinified adhesives prepared by phenolysis and blended with a crosslinking agent (polymeric MDI) (Values in parentheses show number of test specimens giving same adhesion strength.)

that a glue line temperature slightly higher than 130°C can be attained just after 1 min of hot pressing even when the hot press temperature was set at 140°C. Comparing the data shown in Figs. 2, 5 and 6, the effect of the thickness of wooden adherend on the value of glue line temperature attained, becomes apparent. From this examination it is concluded that hot press conditions of 170° C for 22 min are necessary in order to get enough glue line temperature for the curing of adhesive, when gluing of wood specimen with 1 cm thickness is considered. Then, the phenol-hydroxyethylated wood adhesive prepared by phenolysis in the presence of 4 wt% hydrochloric acid of phenol was tested at press temperature of 170°C for 22 min. The results showed that dry adhesive strength is around 174 kgf/cm^2 and almost 100% failure. What is important is that the 'boil-dry-boil' cycle test became more satisfactory. That is, average shear adhesive strength of 40 kgf/cm^2 as well as average wood failure of about 100% could be obtained. Furthermore, some of the test specimens showed shear adhesive strength more than 60 kgf/cm^2, that is higher than the JIS specification (60 kgf/cm^2).

These results seem prospective, but to get a better water-proof gluability, effect of addition of crosslinking agent which can react with hydroxyl groups of wood components was examined as described in the experimental section. In this case, care was taken to complete the application of the adhesive to test specimens within 10 min after mixing with crosslinking agent. Curing was carried out by hot pressing at 170°C for 22 min. Both, the dry adhesive strength as well as the water-proof gluability were tested by using 12 specimens for each test. All the data are plotted in Fig. 7. It was found that the wood failure becomes almost 100%. From the Figure, it is known that the adhesive strength also exceeds the JIS specification in all the cases.

CONCLUSION

From these results, it can be concluded that the present adhesives prepared by replacing more than half parts of phenol with hydroxyethylated wood can be used as prospective glues, when adequate conditions are adopted. It is also found that the gluability can be further enhanced by addition of the appropriate crosslinking agent.

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