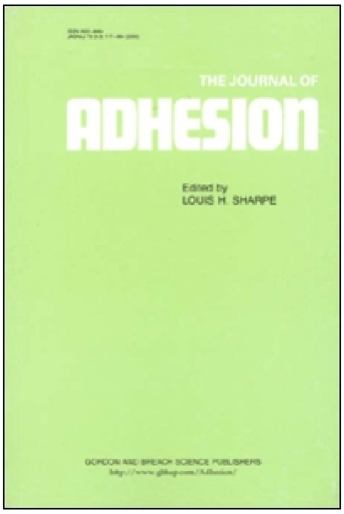

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Thermosetting Adhesive Based on Tannin and Poly(*N*-Hydroxymethyl Acrylamide)

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A thermosetting adhesive consisting of tannin and poly(N-hydroxymethylacrylamide) was studied. This adhesive is an environmentally friendly one using only water as the solvent and is partly based on a natural product. It showed good bonding strength and water resistance for a wood product although those properties were lower than the level of phenol-formaldehyde resin.

Keywords: Adhesive; NMA; Tannin; Thermosetting; Water-resistance; Wood

INTRODUCTION

Establishing low stress and healthy living conditions in society is an important issue nowadays. Reducing emissions of formaldehyde and other volatile organic compounds (VOCs) is a crucial objective relevant to adhesives used in housing construction. Formaldehyde-based urea and phenolic resins, which have been widely used as wood adhesives for a long time, are based on the formation of methylolated intermediates and their subsequent condensation. Thus, methylolureas or methylolphenols are prepared from formaldehyde and urea or phenol, respectively, in the synthesis of adhesives and either self-condensation or condensation with urea or phenol completes the bonding. Formaldehyde might be released if 1) free formaldehyde exists; 2) it is released during condensation; or 3) unstable CH_2-O-CH_2 linkages break down over time [1].

In this work, we examined the reactivity of a methylol group and studied a condensation type adhesive system consisting of tannin, a

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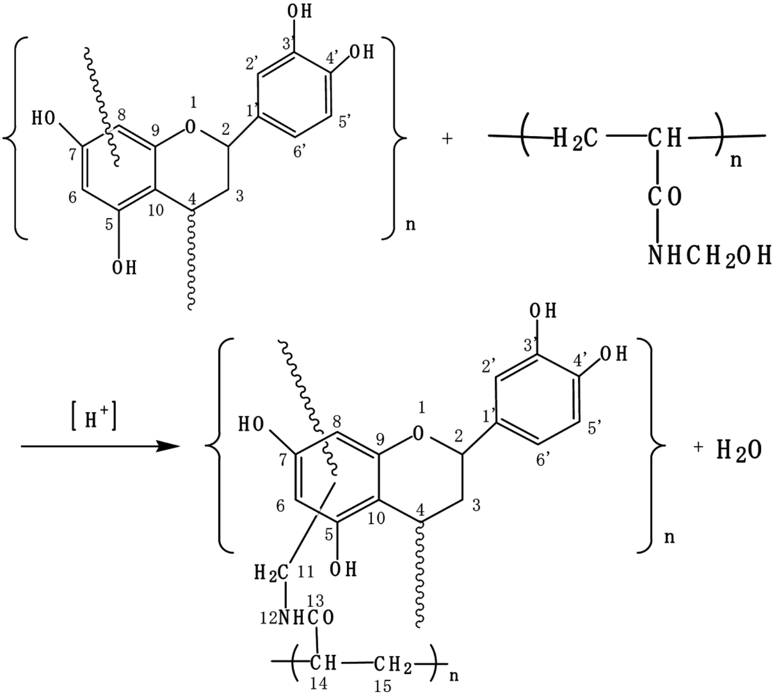

FIGURE 1 Postulated reaction sequeuce of tannin with pNMA.

natural polyphenol [2], and *N*-(hydroxymethyl)acrylamide (NMA) as starting materials. The reported structure of tannin [2] consists of catechin monomer polymerized at the C4, 6, and 8 positions (see Figure 1 for numbering). An expected reaction mechanism of adhesive bonding is depicted in Figure 1. Although tannin and NMA are known to have ability as an adhesive for wood products and have been examined as a partner of phenol resin and co-monomer of vinyl acetate, respectively [2–10], an adhesive based on a combination of the two has not been examined previously. Monomeric NMA was first polymerized, and the performance of an adhesive consisting of NMA polymer (pNMA) and tannin was studied in this report.

EXPERIMENTAL

Materials and Instruments

A commercial product of mimosa tannin (Plytan-AP, Oshika Co., Tokyo, Japan), a condensed tannin, was used, and NMA was a reagent grade chemical (Nakarai Tesque Co., Kyoto, Japan). Other chemicals were commercial products of reagent grade.

The following instruments were used for analyses: ^{13}C-nuclear magnetic resonance spectrometer (JNM-270EX FT-NMR, 270 MHz, JEOL, Tokyo, Japan), HPLC (Shimadzu Co., Model 12 R, Kyoto, Japan), matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS, Kompact MALDI IV of Shimadzu/ Kratos, Kyoto, Japan), an infrared moisture meter (FD-720, Kett Electric Laboratory, Tokyo, Japan), and a Yamazaki type viscosity meter (YV6-S, Yamazaki-seiki Co., Kyoto, Japan).

Preparation of N-Hydroxymethyl Acrylamide Polymer (pNMA)

In a four-neck 500 ml separable flask equipped with a mechanical stirrer, a dropping funnel, and a condenser, *N*-hydroxymethylacrylamide monomer (NMA), 20 g; distilled water, 50 ml; and tetrahydrofuran, 150 ml, were added. The flask was warmed up to 60°C under air with stirring, and a specified amount of 2,2'-azobis(4-methoxy-2,4- dimethylvaleronitrile) (AIBN) was added as a polymerization initiator. The solution changed into a gel-like material in about 20 min. This point was tentatively taken as a standard for the end of reaction. Disappearance of monomer at this point was confirmed by silica gel thin layer chromatography (TLC). After the reaction, the reaction mixture was concentrated under reduced pressure at room temperature, and remaining water in the viscous liquid was removed by freeze-drying to isolate poly(*N*-hydroxymethylacrylamide), pNMA, as a white solid.

Characterization of pNMA

pNMA thus prepared was analyzed by ^{13}C-NMR. The molecular weight was estimated by HPLC with size exclusion (SEC) mode using the following eluting conditions: column, GL W550-S (size, ϕ7.8 mm × 300 mm-long; theoretical plates 9500; exclusion limit molecular weight, 5×10^7, Hitachi, Tokyo, Japan); eluting solvent, water; flow rate, 0.5 ml/mim; under an isocratic condition using a UV detector. As a standard of molecular weight measurement with SEC, Mimosa tannin, the molecular weight of which was determined previously by MALDI-TOF-MS (dithranol as a matrix) [11], was used.

Preparation of Adhesive from Tannin and pNMA, and Determination of Bonding Strength

Adhesive was prepared by mixing aqueous solutions of tannin and pNMA, in specified amounts of components as shown in each figure, at room temperature. The total concentration of organic solids in the adhesive formulations was adjusted to 57% with distilled water. A 1 ml aliquot of 0.5–1 mol/l solution of ammonium chloride, sulfuric acid, or *p*-toluene sulfonic acid was used as a curing agent. The viscosities of adhesive formulations were measured.

The performance of the adhesive was determined by bonding veneers of 1.5 mm thick radiata pine, *Pinus radiate*, to prepare a 3-ply plywood in accordance with JIS K6802 standard [12]. No extenders or fillers were used. The water content of the adherend was determined with five veneers by an infrared moisture meter to be 7.95 ± 0.26%. The adhesive (6.7 g) was uniformly applied over one side of each of two veneers of 15 × 16 cm size, and the coated veneers were placed above and below the uncoated core veneer with the direction of the fiber orthogonal to that in the core. The assembly was cold-pressed for 30 min under a pressure of 1.3 MPa, and then hot-pressed for three minutes under a pressure of 0.73 MPa and at the temperature (25–230°C) indicated in each figure. The following conditions (standard test conditions) were used for bonding test species shown in the figures unless otherwise stated: adhesive preparation, tannin/(pNMA + tannin), 50%; a catalyst, 1 ml of 0.5 mol/l sulfuric acid; press conditions, at 130°C under 0.73 MPa of pressure for 5 min; pNMA, a sample of $\overline{M}_n$ 750.

The cutting of test pieces from a bonded board is shown in Figure 2. Five test pieces 2.5 × 8.0 cm in size were prepared as shown in the figure, and two incisions were made so that the bonding area was 2.5 × 1.3 cm. The mechanical strength of all five test pieces was determined based on JIS K6802 after 48 h of bonding at room temperature (test under normal conditions), or keeping the test pieces in boiling water for 72 h, and cooling to room temperature in cold water (continuous boiling test). The mean values of the experimental results are shown as bar graphs in the figures and error bars indicated in a solid line show the standard deviation. Wood failure was measured with every test piece visually and determined by intervals of 5%. Since this is a rough estimate of bonding, error bars for wood failure are not shown in the figures. Comparable pairs of averages ($p < 0.05$) in the mechanical strength calculated by the Tukey-Kramer test are shown as an alphabetical letter in each column of the figures.

This work involves the following studies: effect of the formulation of tannin and pNMA, the curing catalyst, the change in the degree of polymerization of pNMA, and the press temperature on the bonding strength and also on the stability of the adhesive after storage (storage stability).

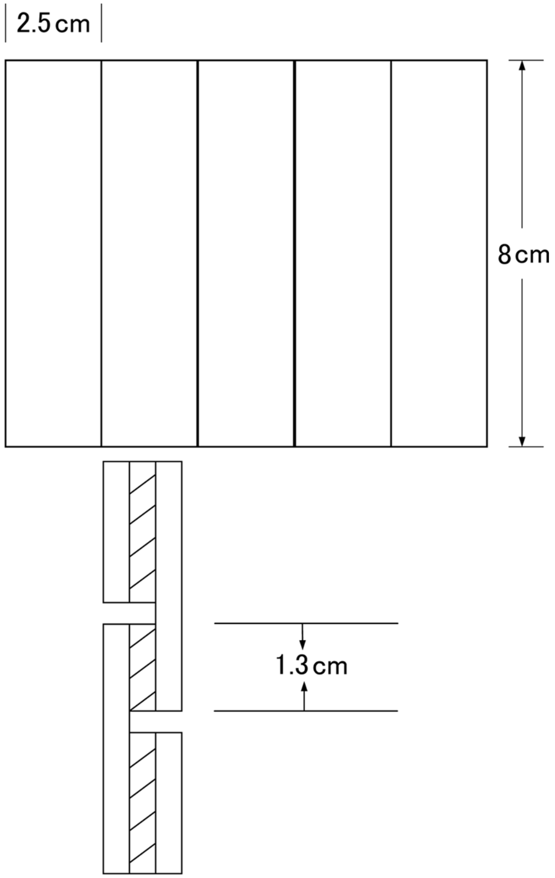

FIGURE 2 Preparation of specimen. Five test pieces of 2.5 × 8.0 cm were cut from a compression molded 3-ply wood, and two incisions were made as shown.

Formaldehyde Emission Test

The emission of formaldehyde from the bonded board was analyzed on the basis of Japanese Agricultural Standard (JAS) test method [13], as follows: Ten test pieces 150 mm long and 50 mm wide were put on a supporting metal fitting placed in a closed container, which contained a crystallizing dish with 300 ml of distilled water in it, and left for 24 h at 20°C. A 2,4-pentandione-ammonium acetate solution was prepared by dissolving the ammonium acetate (75 g, Nakarai Tesque Co., Kyoto, Japan; reagent grade) in 400 ml of distilled water and adding glacial acetic acid (1.5 ml, Nakarai Tesque Co., Kyoto, Japan; reagent grade) and 2,4-pentandione (1 ml, Nakarai Tesque Co., Kyoto, Japan; reagent grade). The solution was well shaken and distilled water was added to make a total volume of 500 ml. The resulting solution was stored in a brown bottle. A standard liquid of formaldehyde was prepared by dilution of the stock solution (37% aqueous solution, Kanto Chemical Co., Tokyo, Japan; extra pure grade) so as to contain 0.1 mg of formaldehyde in 1 ml of solution.

Viscosity

The viscosity coefficient of the synthesized adhesive was determined with a Yamazaki type rotation viscometer to be 40 poise (40 poise = 4000 mPa · s) at 25°C with resin content of the adhesive 57% (solution in water) for the adhesive of 1/1 tannin/pNMA.

RESULTS AND DISCUSSION

Preparation and Analysis of pNMA

Polymerization of NMA was first carried out in distilled water using 30 mg of potassium persulfate as a polymerization initiator, 20 g of NMA, and 100 ml of distilled water at 65°C reacting for 10 min. The reaction mixture gelled completely as the reaction proceeded. Then, the solvent was changed into a mixture of water and THF to control the polymerization. In this medium, homogenous polymerization proceeded smoothly and the solution was cloudy at the initial stage of the polymerization reaction. However, it changed into a gel-like viscous state after the reaction time of 20 min. A white solid was isolated in a nearly quantitative yield after freeze-drying the reaction mixture, which was soluble in water. The polymer did not re-dissolve in water or H_2O-THF when the reaction medium was removed by vacuum distillation under heat. This result suggests that the polymer chain might entangle and that cross-linking [3] and/or intermolecular hydrogen bonds developed through vacuum concentration under heat in contrast to the freeze-dried sample, which did not develop much cross-linking or intermolecular hydrogen bonds to generate the polymer network. The yield of isolated polymer was 99%, almost quantitative, regardless of the reaction conditions. ^{13}CNMR spectra of NMA [3] and pNMA are shown in Figures 3 and 4, respectively. ^{13}CNMR of NMA (in DMSO, Figure 3) showed peaks at δ 65.4 (a methylene carbon adjacent to a hydroxyl group), 127.6 (an acrylic CH2=carbon), 131.8 (an acrylic CH=carbon), and 169.5 ppm (a C=O carbon), and ^{13}CNMR of pNMA (in D_2O, Figure 4) showed peaks, at

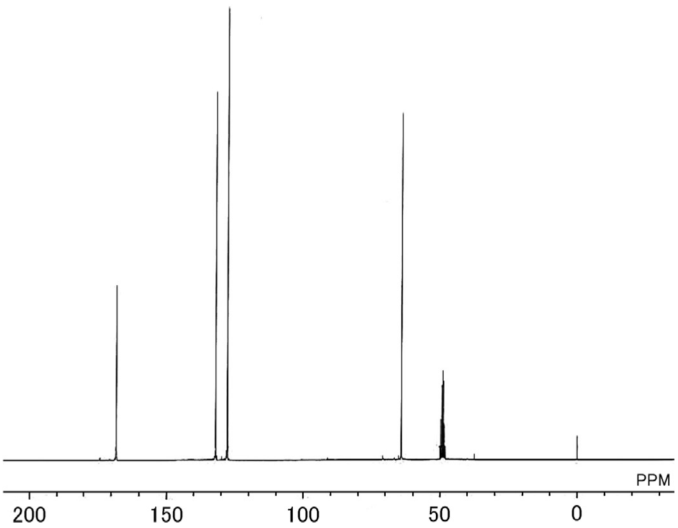

FIGURE 3 ^{13}CNMR spectrum of NMA (methanol-d_4).

δ 36.2 ~ 38.4 (CH_2 carbons in a polymer chain), 44.6 ~ 45.2 (CH carbons in a polymer chain), 65.4 (hydroxylmethylene carbons), and 179.8 ppm (carbonyl carbons of C=O).

Figure 5 shows the SEC chromatogram of pNMA which is dependent on the amount of initiator in the polymerization reaction, together with the SEC of tannin. It shows that the molecular weight

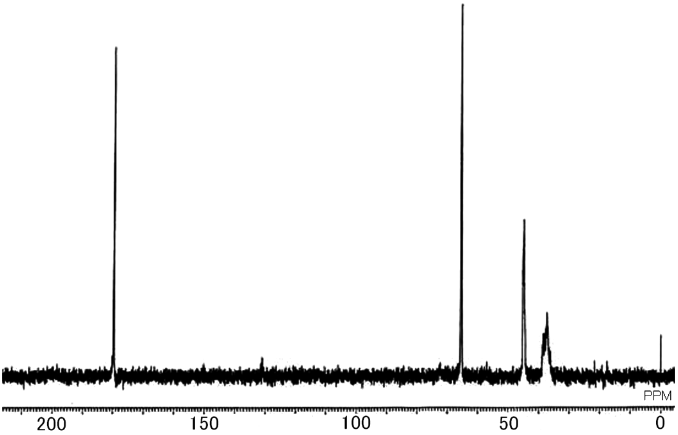

FIGURE 4 ^{13}CNMR spectrum of pNMA (D_2O).

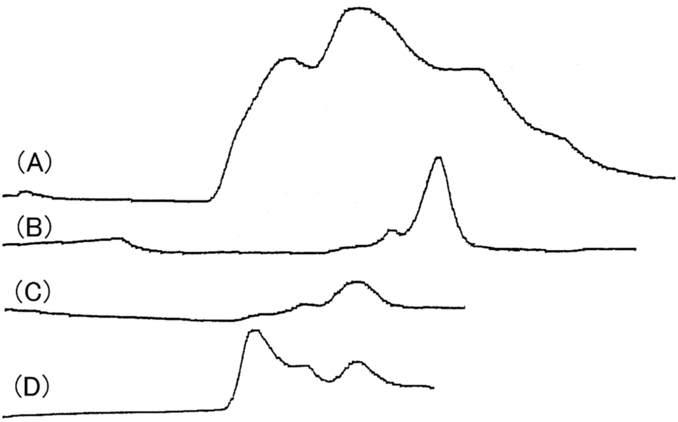

FIGURE 5 SEC chromatogram of pNMA: (A) tannin as the reference; (B) pNMA prepared with 30 mg of AIBN; (C) pNMA prepared with 20 mg of AIBN; (D) pNMA prepared with 10 mg of AIBN.

of polymer was controlled by changing the amount of the initiator, as expected. Since the peaks due to pNMA were not detected successfully by MALDI-TOF-MS, tannin, the MALDI-TOF-MS of which was measured, as reported in Ref. [11], was used as the molecular weight standard of SEC analysis of pNMA as stated already. The main molecular weights were observed at 1451, 1161, and 871 m/e for tannin. Although the relative abundance of the peaks in MALDI-TOF-MS does not necessary correspond to the distribution of the materials, the first peaks on SEC may be tentatively assigned to m/e 1451, the second peak 1161, and the third peak 871. On the basis of the obtained results, pNMA prepared with 30 mg of AIBN is presumed to have a number average molecular weight, $\overline{M}_n$, of about 750, that with 20 mg AIBN corresponds to a $\overline{M}_n$ of 1000, and that with 10 mg AIBN to a $\overline{M}_n$ of about 1500. The molecular weight of the obtained polymer was not high as was seen from the result of SEC. An attempt at polymerization under a nitrogen atmosphere gave a gelled reaction mixture even in H_2O-THF. Since the purpose of this study was to examine a water-soluble adhesive, further attempts at preparation of high-molecular weight pNMA were not made.

Bonding Strength

The influence of the weight percent of tannin in the adhesive (tannin + pNMA) on the bonding strength (Figures 6A and B) showed that the bonding strength is good at 25% of tannin content under normal

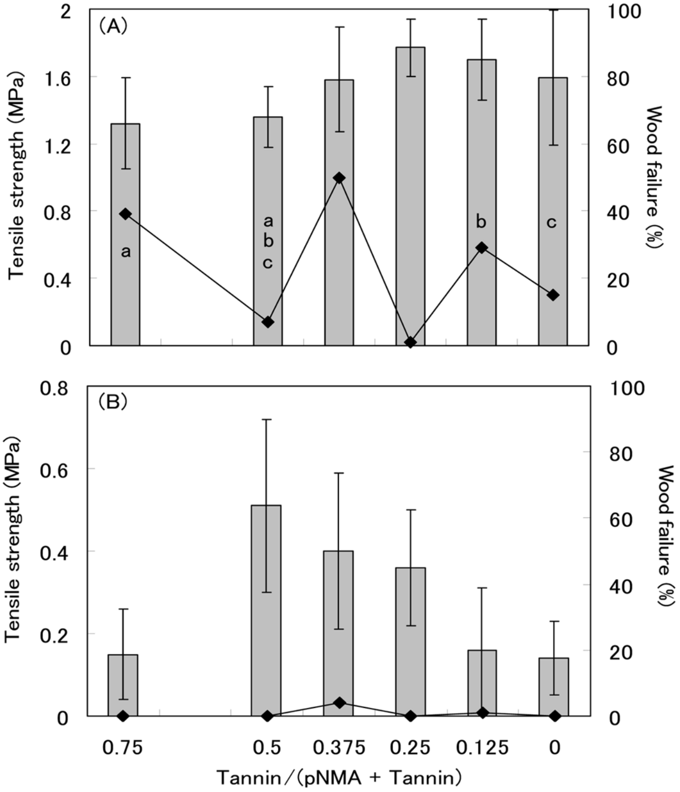

FIGURE 6 Effect of tannin/(pNMA + tannin) weight percent on tensile strength. Bar graph indicates tensile strength and line graph (diamond) indicates wood failure. Error bars show the standard deviations. Alphabetical letter indicates the comparable pair by Tukey-Kramer test. (A) Test under normal conditions, (B) Test under continuous boiling conditions.

test conditions, and the strength after boiling was better with 50% of tannin content. It is frequently observed that bonding strength increases through the boiling test due to post-curing when there is some uncured material remaining in the adhesive. Likewise, some post-curing might have occurred during the continuous boiling conditions for the formulation of 50% tannin, since the observed tendency of strength is contrary to that of normal conditions. The fact that the normal strength was high for the formulation of 25% tannin may show that the influence of pNMA is remarkable, judging from the experimental result that a moderate strength was obtained even with pNMA alone under the normal conditions.

The effect of catalyst was studied using 1 ml of 1 mol/l aqueous solution (sodium hydroxide, ammonium chloride, or *p*-toluene sulfonic acid), and compared with the standard conditions of 0.5 mol/l aqueous sulfuric acid catalyst as shown in Figures 7A and B. It was confirmed that a strongly acidic condition tends to give good bonding strength. High bonding strength was not attained with a weak acid catalyst such as ammonium chloride, but a strong acid such as sulfuric acid

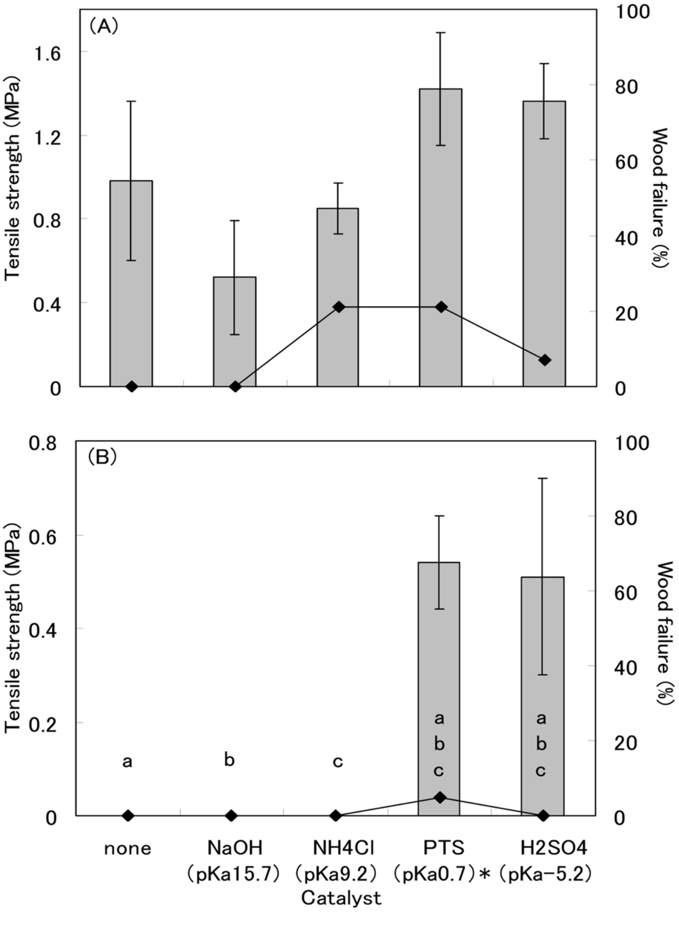

FIGURE 7 Effect of catalyst on the tensile strength. Bar graph indicates tensile strength and line graph (diamond) indicates wood failure. (A) Test under normal conditions, (B) Test under continuous boiling conditions. *The value of bensenesulfonic acid, which is almost the same as PTS.

and *p*-toluene sulfonic acid (PTS) gave good bonding strengths. Since the expected reaction mechanism for condensation is an acid catalyzed dehydration of a methylol group to generate a carbocation intermediate and subsequent electrophilic substitution at the resorcinol ring of the catechin unit by a generated carbocation, it is acceptable that a strong acid which gives a high concentration of protons showed a better catalytic effect than a weak acid, and sodium hydroxide which removes protons of the aromatic alcohol to give a phenolate ion hindered the condensation. Then, it is preferable to use PTS (pKa level is similar to benzenesulfonic acid, which is 0.7 at 25°C) rather than H_2SO_4 (pKa -5.2 at 25°C) because the acidities of the two acids in water do not differ very much due to the leveling effect of the oxonium ion, and the damage to wood is expected by the dehydration effect of remnant sulfuric acid, from the view point of long-term use of bonded wood. To compare the present results of wood bonding with that of phenol resin, PF, the JAS standard for plywood [13] bonded with PF requires a strength of more than 0.7 MPa after continuous boiling in water for 72 h. However, the adhesive reported here showed a little lower strength than the value required by the standard. So, the adhesive consisting of tannin-pNMA showed a fair wood bonding even in the continuous boiling test, but the bonding strength is still lower than that with PF.

The influence of average molecular weight of pNMA on bonding strength is shown in Figures 8A and B. The adhesive using pNMA of molecular weight 1000 gave better strength and was more easily applied on the wood surface. In the radical solution polymerization of pNMA the amount of initiator determines the $\overline{M}_n$. Because the viscosity of the pNMA solution after polymerization with 10 mg of initiator was too high, polymerization using less than 10 mg of initiator was not examined.

The influence of press temperature on bonding strength is shown in Figures 9A and B. The change in strength was small in the test under normal conditions by changing the press temperature from 100 to 180°C. At 230°C press temperature, normal strength decreased, although wood failure increased with increasing press temperature. These results suggest that the test pieces deteriorated at the high pressing temperature of 230°C under acidic conditions.

The results in Figure 9 also suggest that the adhesive can bond effectively even at normal ambient temperature and that bonding develops well at 100°C in the presence of acid catalyst. On the other hand, the important effects of the press temperature and/or cure time for bonding strength are confirmed by the increased strength of water resistance tests with the increase of the press temperature.

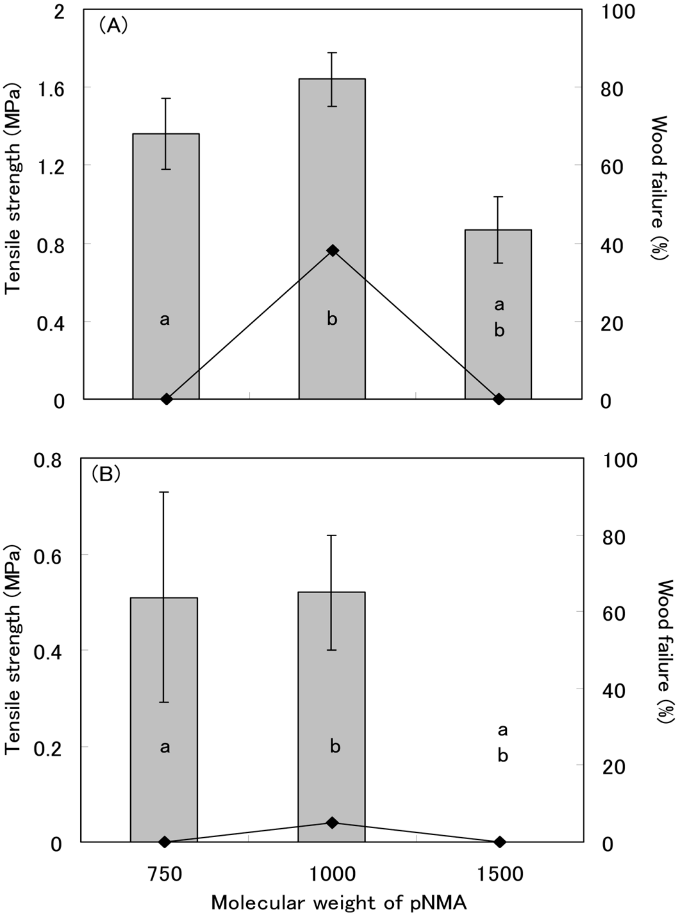

FIGURE 8 Effect of molecular weight of pNMA on tensile strength. Bar graph indicates tensile strength and line graph (diamond) indicates wood failure. (A) Test under normal conditions, B) Test under continuous boiling conditions.

The time-dependent stability of the adhesive was examined by the bonding test after the adhesive was stored for specified periods at an ambient temperature of about 25°C, and the results are shown in Figures 10A and B. The test conditions of bonding were the same as the above standard conditions. There was no change in the bonding strength even after the adhesives were kept for a month, confirming high stability of storage. The small increase in strength observed after 10 or 30 days of storage may be ascribed to an artifact or due to the result of concentration of the adhesive through the evaporation of water.

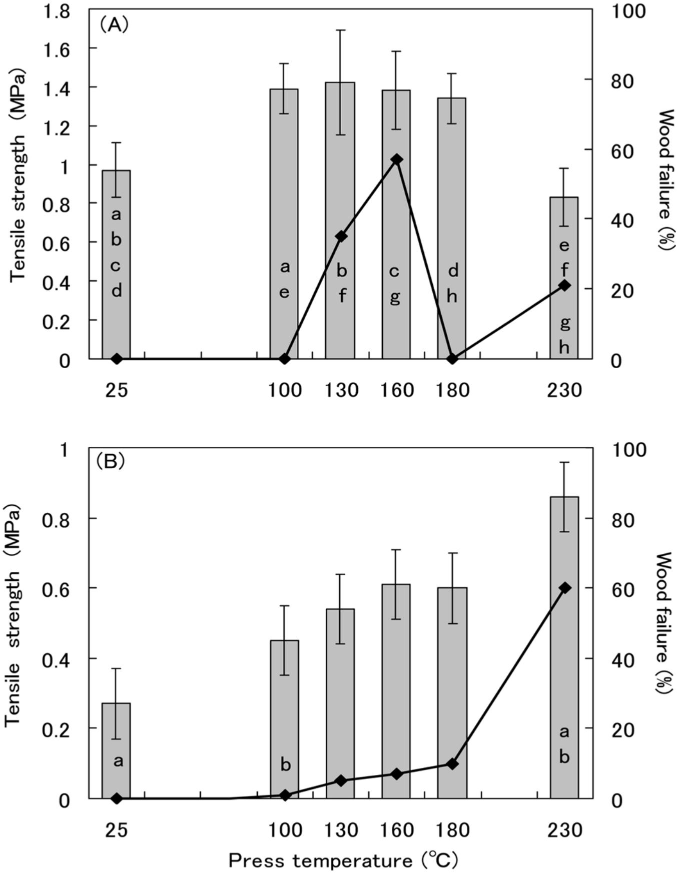

FIGURE 9 Effect of press temperature on tensile strength. Bar graph indicates tensile strength and line graph (diamond) indicates wood failure. (A) Test under normal conditions, (B) Test under continuous boiling conditions.

Thus tannin-pNMA adhesive showed reasonable bonding of wood after 72 h boiling in water. Since tannin has several reactive sites such as C6 and C8 of the resorcinol ring, C4 of chromane ring, and the catechole ring carbons in the constitutional element of catechin, it is expected that a carbocation generated by protonation of a hydroxyl group in *N*-hydroxymethyl acrylamide will react at some of these places, inducing bonding between tannin and pNMA. To elucidate the sites of reaction of catechin, a monomer unit of tannin, with NMA monomer was examined. This is reported in the succeeding paper [11].

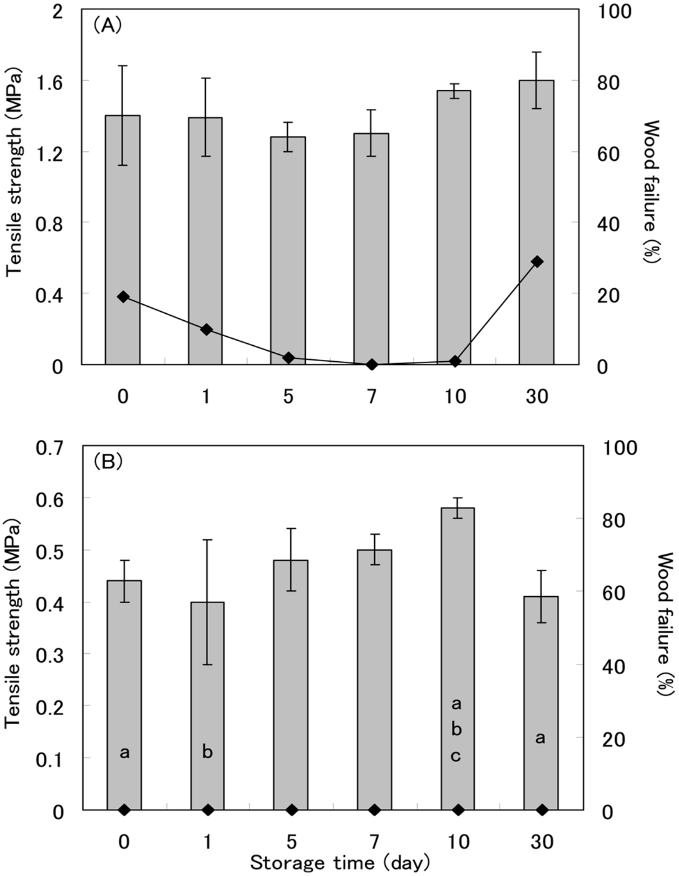

FIGURE 10 Effect of storage time of adhesive on tensile strength. Bar graph indicates tensile strength and line graph (diamond) indicates wood failure. (A) Test under normal conditions, (B) Test under continuous boiling conditions.

Formaldehyde Emission

Although formaldehyde was not used in this adhesive, there is a possibility of formaldehyde release when the *N*-hydroxymethyl compound is heated under the acidic reaction conditions. The result of the formaldehyde emission test indicates that the release from the hot pressed (100°C) sample was 0.45 mg/l, indicating that the emission of formaldehyde is not significant. This value corresponds to F-three stars in the JAS plywood standard.

CONCLUSIONS

In summary, the tannin-NMA adhesive developed in this work has properties suitable for practical use on wood material although it does not reach the level of a phenolic adhesive (0.7 MPa in the 72 h continuous boiling test) [13]. Nevertheless, this is an environmentally friendly adhesive that does not use a solvent other than water and is based in part on natural products.

ACKNOWLEDGMENTS

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