

Preparation and Characterization of Wood Polyalcohol-Based Isocyanate Adhesives

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ABSTRACT: Sugi (*Criptmeria Japonica*) wood meal was liquefied at 150°C with a mixture of poly(ethylene glycol) 400 and glycerin in the presence of a sulfuric acid catalyst. The resulting liquefaction products were used directly to prepare isocyanate adhesives via mixing with polymeric diphenylmethane diisocyanate without the removal of the residue. The properties of the liquefaction products and the performances of bonded plywood were tested. The results showed that the residue content decreased and the hydroxyl value increased as the reaction time increased. The viscosity and weight-average molecular weight significantly changed with the reaction time. All the dry test results of the shear

strength met the Japanese Agricultural Standard (JAS) criteria for plywood. After a cyclic steaming treatment, however, only the plywood bonding with adhesives from the liquefied wood with a reaction time of 1.5 h satisfied the JAS criteria. The wood failure was very low. The emissions of formaldehyde and acetaldehyde were extremely low. Liquefied-wood-based isocyanate adhesives have the potential to become ideal wood adhesives because of their bond durability, safety, and recyclability. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 791–795, 2005

Key words: adhesives; waste; recycling

INTRODUCTION

Recently, the environmental benefits of the effective utilization of waste wood have been attracting attention. Materials made from recycled waste wood, such as solid-wood and plywood panels, have already been used in the particleboard and fiberboard industries. However, once used, wood particles and fibers are difficult to reuse again because of the heavy physical damage. Most of these final wood wastes usually go to thermal recycling as a fuel. The wood-liquefaction technique has the potential to convert the final wood waste and other unused biomass into useful chemical intermediates.^{1–9} Recent intensive studies of wood recycling have resulted in its use as raw materials for adhesives,^{1–5} fibers, carbon fibers,⁶ and so forth.

To promote the development of the liquefaction technique, a novel concept of utilization must be developed for the liquefaction products. Although liquefied wood (LW) in the presence of poly(hydric alcohol) has reportedly been used as a raw material for foams,^{7–9} no report has yet been published on an application for LW-based isocyanate adhesives. How-

ever, the renewable products cannot compete with petroleum products because of their processing cost. It is necessary to find some advantages for the renewable products.

In recent wood adhesives, the intensive regulation of toxic volatile organic compounds such as formaldehyde from wood-based materials has contributed to the resolution of the indoor-air-quality problem.^{10,11} Although formaldehyde-based adhesives have been reformed dramatically to reduce formaldehyde emissions for decades,^{11–15} formaldehyde-free wood adhesives are apparently safer. Water-based polymer-isocyanate adhesives (APIs) were originally developed in Japan as formaldehyde-free adhesives in 1970s.¹⁶ APIs consist of two parts. The main reagent is a mixture of aqueous emulsion polymers such as poly(vinyl acetate), poly(acrylic ester)s, and styrene-butadiene copolymer and/or an aqueous solution such as poly(vinyl alcohol) and a carboxymethylcellulose solution. The curing agent is a diisocyanate compound such as polymeric diphenylmethane diisocyanate (pMDI).¹⁷ APIs have been used mainly for glued laminated timbers and have shown excellent bond performance for 3 decades. In addition, APIs can be applied to veneers with a high moisture content over 15–20%.¹⁷ This makes it possible to use wood efficiently and reduce the drying cost of veneers. Polyalcohol-LW products have similar components to water-based polymers in APIs and are expected to replace them. The LW-based isocyanate adhesives should be able to provide not only safety and bond durability but also recyclability.

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In this study, wood meal was liquefied at 150°C with a mixture of poly(ethylene glycol) 400 (PEG 400) and glycerin with sulfuric acid as a catalyst. Then, the resulting liquefaction products were used to prepare isocyanate adhesives combined with pMDI. Finally, the properties of the liquefaction products and the performances of the bonded plywood were investigated.

EXPERIMENTAL

Materials

Sugi (*Criptmeria Japonica*) chips ground to pass through a 1-mm screen were dried in an oven at 105°C for 12 h before use. The pMDI used here (MR-200, Nippon Polyurethane Industry Co., Ltd., Tokyo, Japan) contained 30.9 wt % NCO groups. Poly(ethylene glycol) [PEG; weight-average molecular weight (M_w) = 400] was extrapure. *N,N*-Dimethylformamide (DMF), acetonitrile, and distilled water were high-performance liquid chromatography (HPLC) grade reagents. All the other chemicals were guaranteed reagents and were used as received. A commercial water-based API (TP-111, Oshika Corp., Tokyo, Japan) was used for comparison with the liquefied-wood-based isocyanate resin (LWI).

Preparation of LW with poly(hydric alcohol)s

The liquefaction reaction of wood was conducted in a separable flask equipped with a stirrer and a reflux condenser. A poly(hydric alcohol) reagent mixture of PEG 400 (157.5 g) and glycerin (67.5 g) at a weight ratio of 7 to 3 and a 98% sulfuric acid catalyst (6.75 g) were premixed thoroughly in the reaction flask, and about one-third wood powder (25.0 g) was added. Then, the reaction flask was immersed in an oil bath preheated at 150 ± 2°C. After some time, the remaining wood powder (50.0 g) was gradually put into the reaction flask. The poly(hydric alcohol) reagent/wood/sulfuric acid weight ratio was 3/1/0.09. After the liquefaction reaction was conducted for a desired period, the flask was immersed in cold water to quench the reaction. An equivalent amount of a 40% sodium hydroxide aqueous solution (13.1 g) was added to neutralize the sulfuric acid to obtain the liquefaction products (LW), which were used to prepare LWIs.

Characterization of LW

Measurement of the residue content

About 5 g of LW was weighed and dissolved in about 70 mL of a dioxane/water binary solvent (dioxane/water = 8/2), the mixture was stirred for 30 min, and then the dilution was filtered through glass filter paper (Toyo GA100) *in vacuo*. The residue was dried to a

constant weight at 105°C in an oven, and then the residue content was calculated.

Measurement of the acid value

About 1 g of LW and 100 g of a dioxane/water (6/4 v/v) binary solvent were titrated with a 0.1N sodium hydroxide solution. The change in the pH was monitored with a 716 DMS Titrino (Metrohm, Ltd., Herisau, Switzerland). The neutralization volume of the sample was obtained from the neutralization curve. The acid value (mg of NaOH/g) was calculated according to the following equation:

$$\text{Acid value (mg of NaOH/g)} = 4.000/V/F/W$$

where V is the consuming volume (mL) of the sodium hydroxide solution at the neutralization point, F is a factor of the 0.1N sodium hydroxide solution, and W is the weight of the sample.

Measurement of the hydroxyl value

About 1 g of LW was first esterified with 25 mL of a phthalic anhydride solution for 2 h at 98 ± 2°C and then cooled to the ambient temperature. After that, 50 mL of dioxane and 25 mL of water were added, and then the mixture was titrated with a 1N sodium hydroxide solution. The change in the pH was monitored with a 716 DMS Titrino (Metrohm). The neutralization volume of the sample was obtained from the neutralization curve. The hydroxyl value (mg of NaOH/g) was calculated according to the following equation:

$$\text{Hydroxyl value (mg of NaOH/g)} = 40.00 \\ \times (B - A)/F/W + \text{Acid value}$$

where A is the volume (mL) of the sodium hydroxide solution consumed at the neutralization point and B is that of the blank solution.

Measurement of the moisture content

The moisture content of LW was determined with a 701 KF Titrino and a 703 Ti Stand (Metrohm) with the Karl Fischer method.

Measurement of the molecular weight determination

The molecular weights and molecular weight distributions of LW were determined at 40°C in DMF as the mobile phase with a Shimadzu LC-6A gel permeation chromatography (GPC) system (Shimadzu Corp., Kyoto, Japan) equipped with two 30-cm polystyrene gel columns in series (Shodex GPC KD 802 and KD 806M). The chromatograms were monitored with a Shimadzu RID-6A differential refractometer detector.

TABLE I
Properties of Polyalcohol-LW Products

Samples	Reaction time (h)	Hydroxyl value (mg of NaOH/g)	Acid value (mg of NaOH/g)	Moisture content (%)	Viscosity at 25°C (mPa/s)	M_w^a	M_w/M_n^a	Residue content (%)
LW1.5	1.5	208.8	12.9	6.9	4340	4349	7.3	15.7
LW3.0	3.0	219.1	12.9	7.7	2726	6766	10.7	11.9
LW5.0	5.0	273.4	14.4	8.9	1773	9407	13.5	8.7

^a Monodisperse polystyrene standard calibration.

The flowing rate and injection volume were 1.0 mL/min and 20 μ L, respectively. Monodisperse polystyrene (GL Science Inc., Tokyo, Japan) was used as the standard for calibrating the molecular weight.

Measurement of the apparent viscosity

The viscosities of LW were measured with a BH viscosity meter (Toyo Seiki, Seisaku-sho, Ltd., Tokyo, Japan) according to JIS K 6833.

Preparation of the LWI adhesives

The LWI adhesives were prepared via the blending of 100 parts of LWI and 158 parts of pMDI. The total solid content of the LWIs was more than 90%. In contrast, the solid content of the commercial API resin was 66%.

Preparation of the plywood panels and test specimens

Red meranti (*Shorea* spp.) veneers measuring 310 \times 310 \times 1.6 mm were stored at 20°C and 45% relative humidity to reach an approximate equilibrium moisture content of 5%. The veneers were laminated into three-ply plywood panels. Two panels were manufactured for each resin system. Both sides of the core veneers were spread with 166 g/m² of each LWI adhesive or with 250 g/m² of the commercial API. The open assembly time was minimal because the veneers were mounted immediately after the adhesive was spread. The panels were prepressed at 0.98 MPa for 15 min at room temperature and then were pressed at 0.98 MPa at 120°C for 1.6 min.

Ten specimens (150 \times 50 mm) for the measurement of the formaldehyde emission and 20 specimens (80 \times 25 mm) for the shear strength test were cut from two duplicate panels.

Measurement of the tensile shear strength

The tensile shear bond strength was determined in accordance with the Japanese Agricultural Standard (JAS) for plywood (normal state and cyclic steaming treatment) with a Toyo Seiki Stograph W tensile tester. In the normal state test, the test specimens were

stored in a conditioned room at 20°C for at least 24 h. In the cyclic steaming test, the specimens were immersed in water at room temperature for at least 2 h and then were put in a pressure cooker with distilled water. The pressure cooker was heated to 130 \pm 3°C and kept at that temperature for 2 h. After cooling, the specimens were immersed in flowing water for 1 h, and then the same steaming procedure was repeated.

Measurement of the aldehyde emission

The formaldehyde emission from plywood bonded with the LWI adhesive was determined in accordance with JAS for plywood. Ten specimens were set in a 10-L glass desiccator with 300 mL of distilled water at 20°C for 24 h. The aldehydes were analyzed in accordance with the procedure reported in a previous article.¹⁸ The aldehydes absorbed in the water were derivatized by the reaction with a 2,4-dinitrophenylhydrazine acid solution. The mixture was diluted with acetonitrile, and the solution was subjected to HPLC analysis as follows. The concentration of absorbed aldehydes in the water was determined by HPLC with a Shimadzu VP-10 system equipped with a UV absorbance detector and two Shinwa-Kako ODSII columns (3.2-mm i.d. \times 150 mm). The eluent was composed of 60% acetonitrile and 40% water. The flowing rate of the eluent and the injection volume of the samples were 1.0 mL/min and 20 μ L, respectively.

RESULTS AND DISCUSSION

Behavior of wood liquefaction

The efficiency of wood liquefaction is one of the most important factors to consider for making the process practical for industry. The solid residue content in the reaction products of wood liquefaction is used as an index of the efficiency of wood liquefaction. As shown in Table I, the residue content of the product gradually decreased in the initial stage. After 1.5 h, the residue decreased quite slowly with the reaction time.

In fact, the residue content would be much lower if based not on the weight of the initial wood but on the weight of the resulting liquefaction products. When the LW product is applied for polyurethane foams, it is necessary to remove the solid residue because it

affects the foam production and its performance. This additional step is one of the drawbacks for recyclability and causes high costs for foam manufacturing from an industrial viewpoint. However, for adhesive applications of LW, a small part of the solid residue could be used. The residue content and the size of the solid residue of LW in this study were small enough (<0.5 mm) to be applied for an adhesive use. Therefore, the liquefaction products in this study could be used directly to prepare isocyanate adhesives without further removal of the residue.

Characterization of LW

Table I summarizes the basic properties of the LW products. The production of acidic substances (acid values) was measured during the liquefaction. The acid amount was stable vis-a-vis the reaction time. This result can be ascribed to the presence of acidic substances in the wood components and the oxidation of the saccharides during liquefaction.^{7,8}

It was reported that the hydroxyl value decreased with increasing reaction time.⁷⁻⁹ The reason was apparently the reaction between PEG/glycerin and dissolved wood components. In this study, however, the hydroxyl value increased with the reaction time. Although the reason that the hydroxyl value increased is unclear, it may be related to the constant moisture content (ca. 7-9%) in the reaction system.

In contrast to the acid value and moisture content, the viscosity and M_w significantly changed with the reaction time. There was an inverse relationship between the viscosity and M_w ; that is, the viscosity increased as M_w decreased. However, during the liquefaction, the components with higher M_w 's increased and the components with lower M_w 's decreased with the reaction time (the GPC profiles are not shown); as a result, M_w and the molecular dispersion index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] increased in the liquefac-

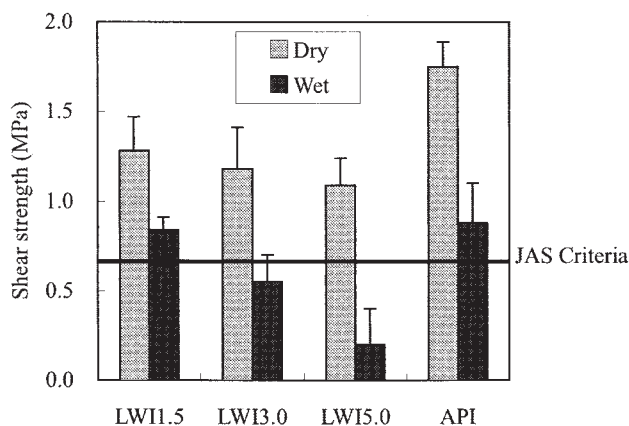


Figure 1 Shear strength of plywood bonded with LWIs and a commercial API resin.

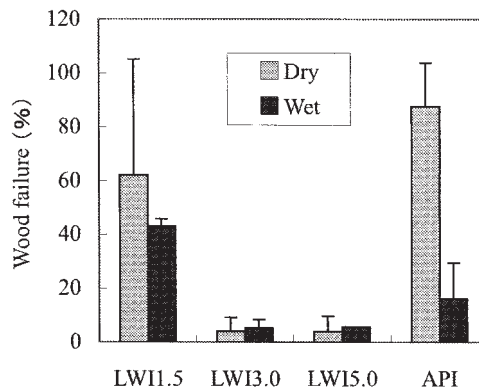


Figure 2 Wood failure of plywood bonded with LWIs and a commercial API resin.

tion products. It is probable that the recondensation of LW products and phase separation between the liquid state and solid residue progressed with the reaction time 3.

Evaluation of the bond performance

The test results for the tensile shear strength and wood failure for the plywood bonded with the LWI adhesives are illustrated in Figures 1 and 2, respectively.

The shear strength in the normal dry state in all the samples met the JAS criteria for red meranti (0.7 MPa). After the cyclic steaming treatment, however, only the wet shear strengths of plywood bonding with the LWI with a liquefaction time of 1.5 h (LWI1.5) exceeded the JAS criteria. The wet share strengths of LWIs apparently decreased as the reaction time increased. The characterization of LW suggests that the lower viscosity of LW3.0 and LW5.0 may have caused overpermeation of adhesives through the wood surface and reduced the share strength in the wet state.

In addition, it is well known that isocyanate adhesives are still not major adhesives for plywood manufacture,¹¹ mainly because of adhesion between the isocyanate adhesives and heat panels.¹⁹ In this study, the phenomenon of plywood sticking to heat panels was observed after hot pressing when the API resin was used. However, with the LWI adhesives prepared in this study, no adhesion problem between the API and the heat panel was found at any stage of the plywood-panel formation process. Although the reason for the phenomenon is unclear, less stickiness to the heat panel would be an advantage of the spread widely use in the plywood industry.

As shown in Figure 2, the wood failure of plywood bonded with LWIs was extremely low, except for the dry wood failure of LWI1.5. It is notable that the wet wood failure of the commercial API was also low, although its dry test results were good. It is necessary to improve the bond performance to use the LWI in the plywood industry.

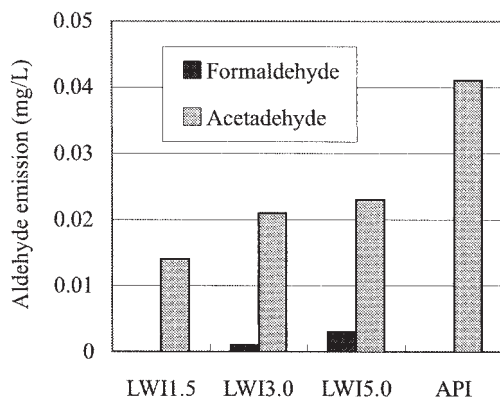


Figure 3 Formaldehyde and acetaldehyde emissions from plywood bonded with LWIs and a commercial API resin.

Aldehyde emission

The emission of volatile organic compounds such as formaldehyde from wood-based materials has become a serious concern. One of the great benefits of using isocyanate adhesives is no inclusion of formaldehyde. Acetaldehyde is also listed as a toxic organic compound in a guideline to indoor-air quality in Japan.²⁰ Acetaldehyde is known to be produced easily by the hydrolysis of vinyl acetate monomer in vinyl acetate polymers,²¹ which are partially used in commercial API resins.¹⁷ Therefore, formaldehyde and acetaldehyde emissions from plywood bonded with the LWIs and commercial API resin were investigated. As shown in Figure 3, the emissions of formaldehyde from the plywood manufactured with isocyanate resins were extremely low in comparison with the JAS severest formaldehyde emission grade F☆☆☆☆ (<0.01 mg/L, as measured by the JAS desiccator method); this is one of the safety advantages of isocyanate binders for wood-based materials. It can be said that the LWI adhesives are totally harmless with respect to formaldehyde emissions.

The emission of acetaldehyde was detected in all plywood samples in this study. In particular, the acetaldehyde emission from the plywood with the commercial API resin was determined to be about 0.04 mg/L. It is difficult to say whether this value is harmless or not because no grade of acetaldehyde emission from wood-based materials has been defined in any standards. It seems that the value is lower than that of other wood-based materials obtained by the same method.¹⁸

The formaldehyde and acetaldehyde emissions from the plywood with LWIs increased as the liquefaction time increased. Because no formaldehyde, acetaldehyde, or vinyl acetate were included in the LWI adhesives as raw materials, it is likely that formaldehyde and acetaldehyde were produced in the process of wood liquefaction.

With the ever-increasing demand for healthy wood products being greater now than ever before, isocyanate resin has been considered an alternative for plywood

adhesives because of its excellent properties and no emission of formaldehyde. In addition, if the LWI adhesives as a material recycling system works in the future, recyclability will join bond durability and safety as major advantages of this material.

CONCLUSIONS

Wood powder was liquefied at 150°C with a mixture of PEG 400 and glycerin with sulfuric acid as a catalyst. As the reaction time increased, the residue content decreased and the hydroxyl value increased, and there were significant changes in the viscosity and M_w . An inverse relationship between the viscosity and M_w was found because of the recondensation of LW products. Acidic substances were produced during the liquefaction. The LWI adhesives were prepared via mixing with pMDI. The results of the bond evaluation of plywood bonded with the LWIs showed that all the dry tests of the shear strength met the JAS criteria. After the cyclic steaming treatment, however, only the wet shear strengths of plywood bonding with LWI1.5 satisfied the JAS criteria. The emissions of formaldehyde and acetaldehyde were extremely low. The safety, durability, and recyclability of the LWI adhesives will inevitably become advantages in the future.

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