

Synthesis of Wood-Based Epoxy Resins and Their Mechanical and Adhesive Properties

Hajime Kishi, Akira Fujita, Hikaru Miyazaki, Satoshi Matsuda, Atsushi Murakami

Graduate School of Engineering, Himeji Institute of Technology, University of Hyogo, 2167, Shosha, Himeji, Hyogo 671-2201, Japan

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ABSTRACT: Wood-based epoxy resins were synthesized from resorcinol-liquefied wood. Wood was first liquefied in the presence of resorcinol with or without a sulfuric acid catalyst at high temperature. Because of the hydroxyl groups, the resorcinol-liquefied wood was considered as a precursor for synthesizing wood-based epoxy resin. Namely, the phenolic OH groups of the liquefied wood reacted with epichlorohydrin under alkali condition. By the glycidyl etherification, epoxy functionality was introduced to the liquefied wood. The epoxy functionality of the resins was controlled by the concentration of phenolic OH groups in the liquefied wood, which would be a dominant factor for crosslink density and properties of the cured epoxy resins. The flexural strength

(150–180 MPa) and the modulus of elasticity (3.2 GPa) of the highly crosslinked wood-based epoxy resin were equivalent to those of the commercially available epoxy resin, diglycidyl ether of bisphenol A (DGEBA). Also, the shear adhesive strength of the wood-based epoxy resin was higher than that of DGEBA when plywood was used as the adhesive substrates. The mechanical and adhesive properties suggested that the wood-based epoxy resins would be well suited for matrix resins of natural plant-fiber reinforced composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2285–2292, 2006

Key words: biopolymers; resins; strength; adhesives; composites

INTRODUCTION

It is essential that industrial systems respect anti-global-warming restrictions. An effective use of plant biomass should be an ideal replacement for fossil-fuel resources. Moreover, in contrast to fossil-fuel resources, plant biomass is a renewable resource, which is another advantage. Therefore, much effort has been devoted to utilizing disposed biomass as a valuable resource for polymers and chemicals.

The liquefaction of wood in the presence of phenols or alcohols has been intensively studied by Shiraishi et al.^{1–6} Liquefied wood has a high reactivity due to the large amount of phenolic OH groups and alcoholic OH groups. Using these functional groups, liquefied wood can be converted to phenolic resins and polyurethane forms.^{7–10} Liquefied wood has further potential and may be used as a resource for other valuable biomass-based materials.

The epoxy-resin family has good mechanical and adhesive performances, and is widely used in various fields, for example, as adhesives, coatings, and matrix resins of composites. The first objective of this study is to synthesize wood-based epoxy resins using liquefied wood as the precursor of the resin. The second objective is to evaluate the mechanical and adhesive

properties of the wood-based epoxy resins in order to clarify the potential of further applications.

EXPERIMENTAL

Materials

The wood sample used was 20–80 mesh wood meal from German spruce (*Picea abies*). Resorcinol, epichlorohydrin, and all other chemicals for liquefaction of wood and synthesis of wood-based epoxy resins were of reagent grade (from Wako Pure Chemical Industries, Ltd., Osaka, Japan), and were used without further purification.

A mixture of diglycidyl ether of bisphenol A oligomers [Ep828 : Ep1001 = 7 : 3 in weight ratio; both grades were produced by Japan Epoxy Resin Inc. (Tokyo, Japan)] was used as a reference epoxy resin.

The resins were cured with a stoichiometric amount of 4,4'-diamino diphenyl methane (DDM).

Synthesis of wood-based epoxy resins

Liquefaction of wood

Wood-based epoxy resins were attained via the following two steps. The first step was the liquefaction of the wood and the second step was the synthesis of epoxy resins from the liquefied wood.

Two methods, namely, the noncatalyzed method and the acid-catalyzed method, were used for the

Correspondence to: H. Kishi (kishi@eng.u-hyogo.ac.jp).

liquefaction of wood. For the noncatalyzed method, the wood was liquefied with resorcinol in a pressure-proof reaction tube (TVS-1 type, Taiatsu Glass Industry Inc., Tokyo, Japan) made of SUS-316 stainless steel.^{1,2} The ratio of resorcinol to wood was 1 or 2, and the liquefaction time was varied from 0.5 to 6 h at 250°C. In the mean time, for the acid-catalyzed method, the wood was liquefied by a reaction with resorcinol and a small amount of sulfuric acid (resorcinol:sulfuric acid with a 100 : 3 weight ratio) in a flask at 150°C.⁴ The ratio of resorcinol to wood ratio was 2, and the liquefaction time was varied from 0.5 to 4 h.

In order to quantify the insoluble residue, the black liquid after the liquefied treatment was diluted 20 times with 1,4-dioxane, and filtered with a glass-fiber filter (Toyo GA-100, Toyo Roshi, Ltd., Tochigi, Japan) that is 1 μm particle-retainable. After drying in an oven at 80°C, the dioxane-insoluble residue was weighed. The amounts of the residue are expressed as weight percents on the basis of the wood samples used.

Glycidyl etherification of liquefied wood

The route for the synthesis of wood-based epoxy resins was basically same as the general synthesis method for commercially available epoxy resins. Namely, the liquefied wood and epichlorohydrin were put into a glass flask and the temperature was raised to 100°C while stirring. The amount of epichlorohydrin was set as the molar ratio of epichlorohydrin for resorcinol in the liquefied wood was 10, which means the epichlorohydrin was put in the reaction system excessively. Next, 50 w/w % sodium hydroxide (NaOH) aqueous solution, corresponding to twice the molar ratio compared to the phenolic OH groups in resorcinol, was slowly added to the composition using a dropping funnel while stirring. The flask was kept at the same temperature for 2.5 h in total to achieve the addition reaction of epichlorohydrin and the ring formation of epoxy groups.

The reacted products were diluted 10 times with acetone, and salts as by-products were filtered out with a glass-fiber filter (Toyo GA-100 as above; 1 μm particle-retainable). The acetone and nonreacted excess epichlorohydrin in the filtered resin solution were evaporated using a rotary evaporator at 80°C under reduced pressure. Then, the wood-based epoxy resins remained in the flask of the evaporator.

Measurement for epoxy equivalent and epoxy index

The epoxy equivalent of synthesized resin was determined according to JIS K7236, from which the epoxy index (epoxide equivalent/kg resin) was calculated.

Gel permeation chromatography

The molecular weight distributions of the liquefied wood and the synthesized wood-based epoxy resins were determined using gel permeation chromatography (GPC, PU-2080 HPLC system using the JASCO-Borwin-GPC program), equipped with columns, Shodex KF-802 and KF-803 (Tokyo, Japan). Tetrahydrofuran (THF) was used as the solvent. The average molecular weights were calibrated using monodispersed polystyrene standards.

FT-IR analyses

The infrared (IR) absorption spectra of the samples were measured using an FT-IR 4100 spectrometer (JASCO Corporation, Tokyo, Japan) using either the KBr-pellet method or the liquid thin-layer method.

Curing of resins

In order to prepare cured resin specimens, mixtures of epoxy resin and DDM were first heated to 80°C so as to lower the viscosity of the resin compositions, thus making it easier for the DDM particles to disperse. Then, the resin compositions were held at 60°C under a vacuum in order to de-gas them. The resin compositions were then poured into preheated silicone-coated molds and cured at 130°C for 4 h then at 150°C for 2 h. Test specimens were machined from the 2-mm-thick cured plaques.

Dynamic mechanical analyses

The temperature dependencies of the viscoelastic properties (storage modulus E' and mechanical loss tangent $\tan\delta$) of the cured resins were evaluated via dynamic mechanical analysis (DMA) in the bending mode using a dynamic frequency of 1 Hz. The instrument used was a DMS6100 (Seiko Instruments, Inc., Chiba, Japan). Cured resin specimens with length of 50 mm, width of 10 mm, and thickness of 2 mm were machined from 2-mm-thick cured plaques. The samples were tested over a temperature range between -100°C and 180°C with a heating rate of 2°C/min. The glass transition temperatures (T_g) and rubbery plateau values of the storage modulus (E'_r) were determined. T_g was defined as the temperature where the tangent line of E'_r in the glassy region and the tangent line of E'_r in the transition region intersect. From the E'_r , the molecular weight between crosslinks, M_c , of cured resins was determined using the following relationship (1)¹¹

$$M_c = 3\phi\rho RT/Er', \quad (1)$$

where $\phi = 1.3$ as a front factor, $\rho = 1.2 \text{ g/cm}^3$ as a density of cured resins, R is a gas constant, and T is

the absolute temperature where E' reached the rubbery plateau region.

Flexural tests for cured resins and composites

The flexural tests for the cured resins and the composites were conducted in the three point bending (3PB) mode with a strain rate of 5 mm/min at 25°C. Specimens with length of 80 mm, width of 10 mm, and thickness of 2 mm were machined from 2-mm-thick cured plaques.

Shear adhesive tests

The tensile shear adhesive strength of the epoxy resins was evaluated using the test machine "INTESCO" from INTESCO Co., Ltd. (Chiba, Japan) in accordance with JIS K 6850 at a crosshead speed of 10 mm/min at 25°C. Plywood plates or steel plates were applied as the substrates for the adhesive tests.

Fabrication of flax-fiber reinforced wood-based epoxy composites

First, uncured resin films composed of mixtures of epoxy resin and DDM were coated on release papers. Additionally, flax fiber mats were cut into 90-mm squares. Each cut fiber mat was placed between two resin films and pressed to make a fiber/resin prepreg. Next, the eight prepregs were laid on top of each other and precompact in a nylon-bag sheet under vacuum pressure. The precompact prepregs were placed in a hot-press machine and cured. The curing condition for the composites was at 130°C for 4 h and 150°C for 2 h under 10 MPa pressure. Test specimens were cut with a diamond saw from the cured composites.

Scanning electron microscopy observation

The fractured surfaces of the biomass composites after flexural tests were observed using a scanning electron microscope (SEM) "KEYENCE VE-7800" from (KEYENCE Co., Ltd., Osaka, Japan). The samples were mounted on brass stubs and were coated with a thin layer of gold using an ion sputter coater "JFC-1100E" made by JEOL (Tokyo, Japan).

RESULTS

Synthesis of wood-based epoxy resins

Wood meal was liquefied by the reaction with resorcinol. The black, highly viscous liquid was considered as a precursor of the wood-based epoxy resin, because the reacted compound would include considerable amount of hydroxyl groups, as the reactive sites originated from the wood and resorcinol.

Figure 1 shows the relationship between the amount of the insoluble residue and the heating time both for noncatalyzed liquefaction and acid-catalyzed liquefaction. About 1.5 to 2 h reaction time gave the minimum value on the insoluble residue. More than 2 h of heating resulted in increased insoluble residue, which would indicate that recondensation of components from degraded wood (polysaccharide and lignin) had occurred.^{1,4,12}

Wood-based epoxy resins were synthesized using the procedure as described above. Figure 2 shows the change of state of the materials by epoxidation reaction. Figure 2(a) shows the resorcinol-liquefied wood before reaction with epichlorohydrin. This liquefied wood as a resin precursor was highly viscous. Figure 2(b) shows the synthesized liquefied wood-based resin after reaction with epichlorohydrin. The resin had some viscosity but was in a liquid state at room temperature, which was desirable for use as an adhesive resin.

Figure 3 shows the relationship between the hydroxyl value of the liquefied wood and the heating time at 250°C for the liquefaction with resorcinol. The hydroxyl value became reduced as the heating time was extended, probably due to heat decomposition and recondensation of the molecular structure.^{1,12} Figure 3 also shows the epoxy index of the epoxy resin synthesized from the corresponding liquefied wood. The epoxy index became also reduced as the heating time was extended. The synthesis route of the wood-based epoxy resins appeared to be glycidyl etherification for the phenolic OH groups. The epoxy functionality shown as the epoxy index would be caused by the concentration of phenolic OH groups in liquefied wood as the precursors.

Figure 4 shows the IR spectra of the wood meal, the resorcinol liquefied wood, and the liquefied wood-based resin. The peak of 910 cm^{-1} in the spectra shows the vibration of the epoxy groups, which indicates the wood-based resin possesses epoxy functionality.

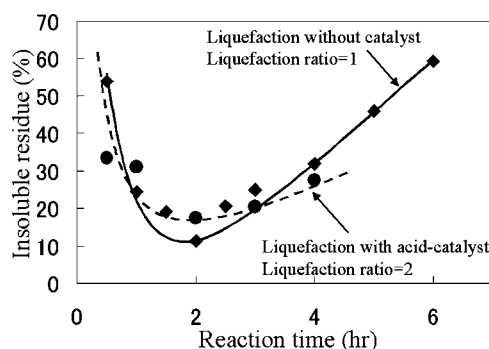


Figure 1 Insoluble residue (%w/w) on resorcinol liquefaction of wood for both the noncatalyzed and acid-catalyzed methods.

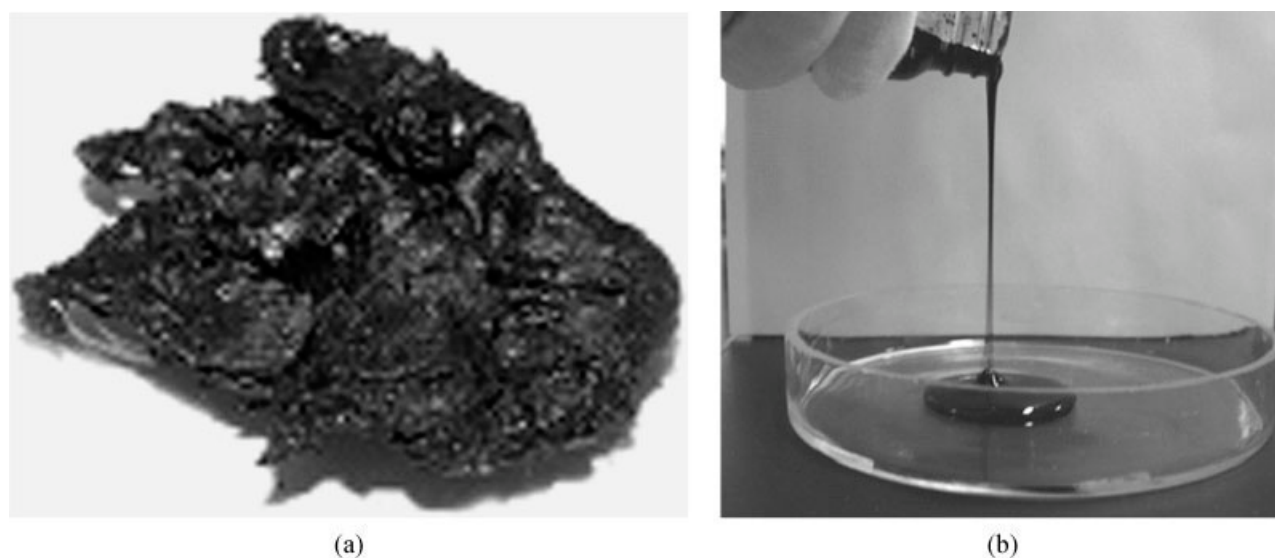


Figure 2 Change of state of the liquefied wood before and after epoxidation reaction: (a) resorcinol-liquefied wood (ratio of resorcinol to wood: 1, liquefaction time: 1.5 h without catalyst at 250°C); (b) synthesized liquefied wood-based resin after reaction with epichlorohydrin.

Figure 5 shows the results of gel permeation chromatography (GPC) for the liquefied wood and for the synthesized resin from the liquefied wood. The number for the average molecular weight of the liquefied wood was about 500 via polystyrene-standards calibration. This has showed that the polymeric wood components, cellulose, hemi-cellulose, and lignin, decomposed to a great extent at 250°C. This depolymerization would have transformed the solid-state wood into the liquid-state material.

The molecular weights before and after the reaction of liquefied wood with epichlorohydrin are also characterized in Figure 5. If the liquefied wood reacts with epichlorohydrin, the molecular weights should increase. The distribution of retention time of the synthesized resin was faster than that of the liquefied wood, which means the average molecular weight of the resin (about 600) became higher than

that of the liquefied wood before reaction with epichlorohydrin (about 500). Moreover, the molecular weight of the resin (about 600) was obviously higher than that of commercially available resorcinol diglycidyl ether ($M_n = 390$).

All the data of the epoxy index by the titration in Figure 3, the IR spectra in Figure 4, and the GPC in Figure 5 suggest that glycidyl etherification reaction for the phenolic OH groups of resorcinol-liquefied wood was achieved and the wood-based epoxy resins were synthesized.

Viscoelastic properties of cured wood-based epoxy resins

Figure 6 shows the dynamic viscoelastic properties of the wood-based epoxy resins cured with DDM. The cured wood-based epoxy resins showed high

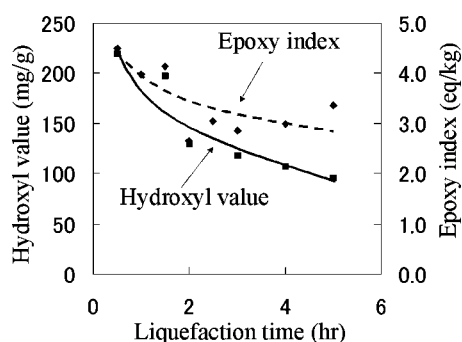


Figure 3 Relationship between the hydroxyl value of the resorcinol-liquefied wood, the epoxy index of the resin synthesized from the liquefied wood, and the liquefaction time at 250°C without catalyst (ratio of resorcinol to wood: 1).

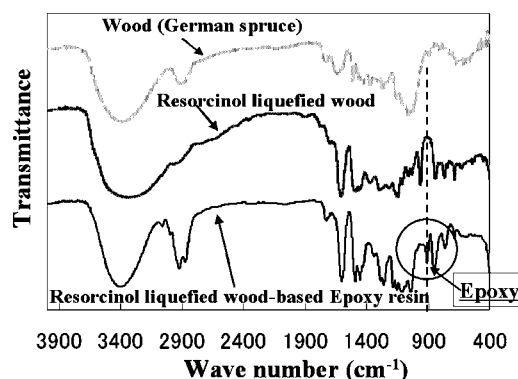


Figure 4 IR spectra of wood meal, resorcinol-liquefied wood without catalyst, and liquefied wood-based epoxy resin, (liquefaction time: 1.5 h, ratio of resorcinol to wood: 1).

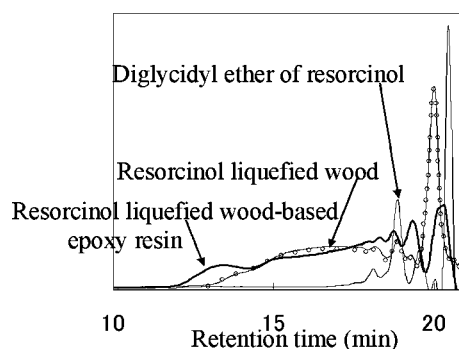


Figure 5 Gel permeation chromatography (GPC) of the liquefied wood without catalyst, the synthesized epoxy resin from the liquefied wood, (liquefaction time: 1.5 h, ratio of resorcinol to wood: 1) and that of diglycidyl ether of resorcinol as a reference material.

stiffness at room temperature and a clear rubbery plateau after T_g . The storage modulus of elasticity of the resorcinol-liquefied wood-based epoxy resin at 25°C was equivalent to that of the bisphenol A type epoxy resin. And the rubbery plateau indicates that a crosslink network structure was surely formed. The T_g of the resorcinol-liquefied wood-based epoxy resin was lower than that of the bisphenol A type epoxy resin. The broad T_g region would mean there is a diversity of crosslink structures in the cured resin, which suggests that the glycidyl-etherified wood components coreacted, and were incorporated into the crosslink structures.

The influence of wood liquefaction time on the viscoelastic properties of the cured wood-based epoxy resins is shown in Figure 7. The cured resin from liquefied wood after 5 h heating at 250°C had a lower T_g and a lower rubbery plateau value than the cured resin from liquefied wood after 1.5 h heating at the same temperature. In general, the rubbery plateau value of the storage modulus is relative to the average crosslink density of cured resins.^{13,14} Next, the molecular weight between crosslinks, M_c , was

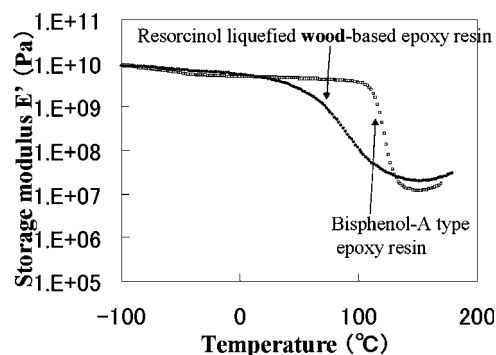


Figure 6 Dynamic viscoelastic properties of the resorcinol-liquefied wood-based epoxy resin and the diglycidyl ether of bisphenol A, cured with DDM, (liquefaction time: 1.5 h without catalyst, ratio of resorcinol to wood: 1).

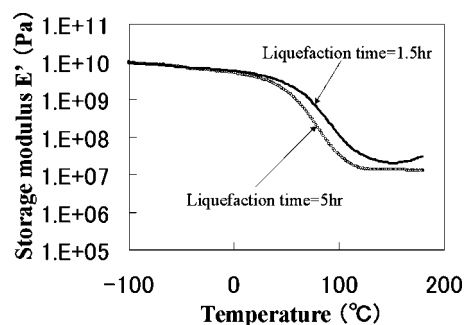


Figure 7 Dynamic viscoelastic properties of the resorcinol-liquefied wood-based epoxy resins cured with DDM (using liquefied wood without catalyst from both 1.5 h and 5 h liquefaction).

then calculated, as described above, from the rubbery plateau values of both the cured resins. The M_c of the resin from 1.5 h liquefaction was 830, and the M_c of the resin from 5 h liquefaction was 1150. These results suggest that the hydroxyl functionality was kept by shortening the liquefaction time, and therefore the epoxy functionality of the synthesized resin was also kept. The crosslink density and the heat resistance of the wood-based epoxy resin would increase with a decrease in the time during which wood-liquefaction was achieved.

Figure 8 shows the effect of the liquefaction ratio (weight ratio of resorcinol/wood for the liquefaction) on the viscoelastic properties of the cured wood-based resins made from the liquefied wood without catalyst in 1.5 h at 250°C. The cured resin made from the liquefied wood with a liquefaction ratio of 2 showed a higher T_g and a higher rubbery plateau than the cured resin from the liquefied wood with a liquefaction ratio of 1. This is probably due to the difference of epoxy functionality as a result of the high content of hydroxyl groups of resorcinol. Figure 8 also shows the influence of the acid-catalyst in the liquefaction on the viscoelastic properties of the

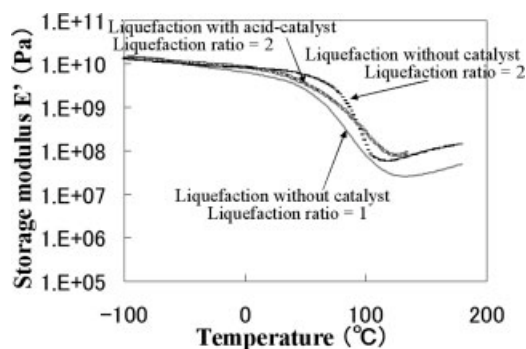


Figure 8 Effects of the liquefaction ratio and the liquefaction catalyst on the dynamic viscoelastic properties of the resorcinol-liquefied wood-based epoxy resins cured with DDM (liquefaction time: 1.5 h).

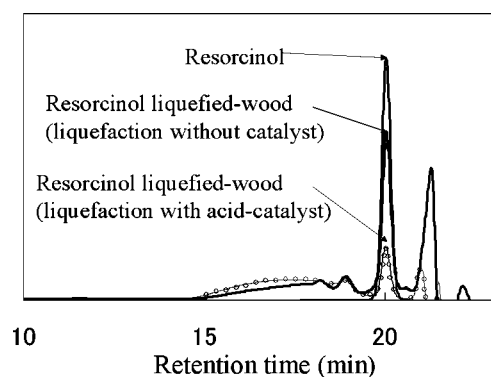


Figure 9 Gel permeation chromatography of two types of resorcinol-liquefied wood (without catalyst or with acid catalyst; liquefaction time: 1.5 h, ratio of resorcinol to wood: 2), and that of sample with original concentration of resorcinol before liquefaction.

cured resins. At the same liquefaction ratio of 2, the resin from the liquefied wood with acid-catalyst indicated a somewhat lower and broader T_g region but a higher rubbery plateau value than the resin from the liquefied wood without catalyst.

In order to clarify the reason for this, GPC analyses were conducted for the sample with the original concentration of resorcinol before the liquefaction, the liquefied sample without catalyst, and the liquefied sample with acid catalyst, as shown in Figure 9. Decrease of the resorcinol peak from the original resorcinol solution indicates the amount of resorcinol that reacted with wood components. The amount of residual-free resorcinol after the liquefaction with acid catalyst was much less than that of free resorcinol after the liquefaction without catalyst, although the chemical compositions of both samples before the reaction were identical (except the catalyst). This indicates that much more resorcinol could react with the wood components during the liquefaction process in case when using acid catalyst. In addition, more components with a relatively fast retention time, that is, with relatively high molecular weights, were included in the liquefied wood sample with acid catalyst in comparison to the liquefied wood sample without catalyst.

These results and discussions suggested that the acid-catalyst method in wood liquefaction allowed more wood components to react with resorcinol than the noncatalyst method, and the wood components were incorporated into the crosslink structures of the cured resins. As the amount of wood components reacted with resorcinol is increased, the diversity of the crosslink structures will also increase, which would lead to the broad T_g region of the cured resin.

It has been reported that the phenolic OH groups were kept in the reaction with wood components.¹⁵ Therefore, the two original hydroxyl groups of resorcinol would be kept after the liquefaction procedure.

If the depolymerized wood components also had hydroxyl groups, the molecules from wood components reacted with resorcinol would become epoxy resins, which would be more than 3-functional after the glycidyl etherification reaction. This would be the reason of the high rubbery plateau value of the cured resin from liquefied wood using acid catalyst.

Flexural properties of cured wood-based epoxy resins

Figure 10 shows the flexural properties (the flexural modulus of elasticity and the flexural strength) of the cured resorcinol-liquefied wood-based epoxy resins from the two types of liquefied wood without catalyst (the resin from 1.5 h and 5 h liquefaction; the liquefaction ratio is 1 in both cases). Both cured resins indicated almost equivalent flexural moduli, but the flexural strength of the cured resin from 1.5 h liquefaction was much higher than that of the cured resin from 5 h liquefaction. This big difference probably came from the difference of the crosslink densities of these cured resins. As mentioned above for Figure 7, the cured resin from 1.5 h liquefaction had a higher crosslink density than the cured resin from 5 h liquefaction.

The flexural strength and flexural moduli of several wood-based epoxy resins at room temperature in comparison with the bisphenol A type epoxy resin are shown in Figure 11. This figure also shows a comparison of the differences between the liquefaction ratio and the liquefaction method. The change of liquefaction ratio from 1 to 2 did not have any significant effect on the flexural strength and the moduli of the cured resins. In addition, the flexural strength and the modulus of the cured resin from the liquefied wood with acid catalyst were slightly lower than those of the cured resin from the liquefied wood without catalyst. This might be an influence of the high content of wood components incorporated into the crosslink structures of the resins using the acid-catalyst method. It should be noted,

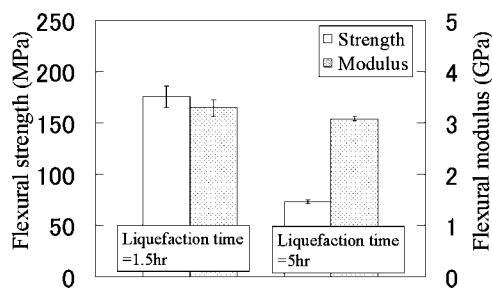


Figure 10 Flexural properties of wood-based epoxy resins from two types of liquefied wood, (using the liquefied wood without catalyst from both 1.5 h and 5 h liquefaction, ratio of resorcinol to wood: 1).

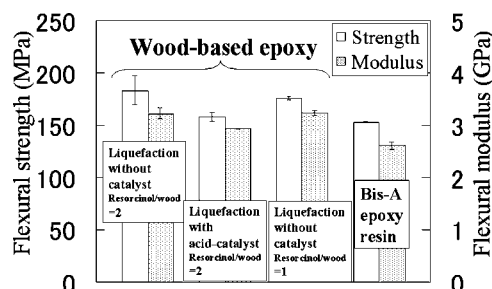


Figure 11 Flexural properties of several wood-based epoxy resins (liquefaction time: 1.5 h) and that of the bisphenol A type epoxy resin as a reference.

however, that these wood-based epoxy resins indicated more than equivalent flexural strength and flexural moduli at room temperature in comparison to the bisphenol A type epoxy resin made from a fossil-fuel resource.

Adhesive properties of wood-based epoxy resins

Figure 12 shows the comparison of the lap shear adhesive strength between the wood-based epoxy resin and the bisphenol A type epoxy resin. When the adhesive substrates were plywood, the shear adhesive strength of the wood-based epoxy resin was higher than that of the bisphenol A type epoxy resin. This would be probably due to the good affinity (wettability) of the wood-based epoxy resins to plywood (biomass material). Regarding the wood-based epoxy resin, the failure part was mainly observed in the plywood, namely the wood-failure part occupied about 60% of the lap joint area. On the other hand, in case of the bisphenol A type epoxy resin, the wood-failure part occupied only about 10% of the lap joint area; in other words, interfacial failure was dominant. This is

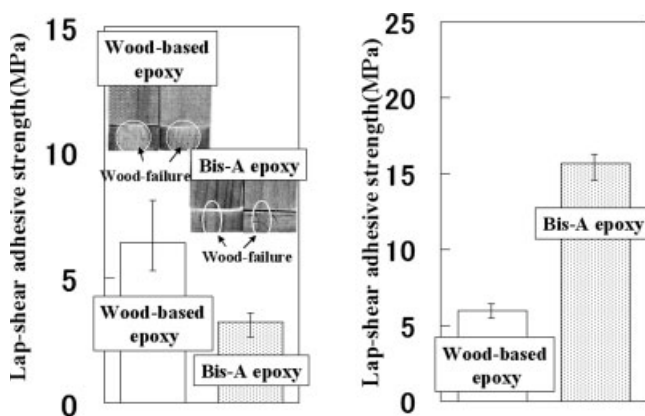


Figure 12 Lap-shear adhesive strengths of the wood-based epoxy resin using the liquefied wood without catalyst (liquefaction time: 1.5 h, ratio of resorcinol to wood: 1) and that of the bisphenol A type epoxy resin. Adhesive substrates: (a) plywood; (b) steel.

evidence that the wood-based epoxy resins have better adhesive properties to plywood than the bisphenol A type epoxy resin. However, when the substrates were steel plates, the shear adhesive strength of the wood-based epoxy resin was lower than that of the bisphenol A type epoxy resin. Interfacial failure was the main failure mode for both resins. The bisphenol A type epoxy resin oligomer has many aliphatic hydroxyl groups in the molecular structure, which would be the main factor for the strong interfacial adhesion to steel with an oxidized surface. In any case, it should be noted that the wood-based epoxy resins have good adhesive strength to plant biomass materials.

Potential of wood-based epoxy resins as matrix resins for biomass composites

In order to find suitable applications for the wood-based resins, a natural plant-fiber reinforced composite consisting of flax fibers and the wood-based epoxy matrix resin was fabricated, as shown in Figure 13. Flexural tests were conducted on the composites and the same fiber reinforced bisphenol A type epoxy composites. Then, the fracture surfaces of the composites were observed using a SEM, as shown in Figure 14. The surfaces of the flax fibers were covered well with the wood-based epoxy resin, and the wood-based resin seems to have better adhesive property to the flax fibers than the bisphenol A type epoxy resin. The wood-based epoxy resin includes molecules from cellulose and lignin that would have similar chemical structures to the components of the flax fibers. This might be one of the reasons that can explain the good adhesive property.

A fractured surface of the flax-fiber reinforced thermoplastic polylactic acid is also shown in Figure 14 as a reference composite. The surface of flax fibers in the fractured composite was very smooth, which suggests that polylactic acid has poor adhesion to the flax

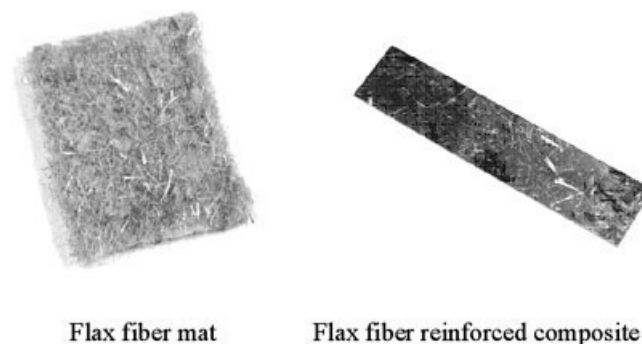


Figure 13 Flax-fiber mat and flax-fiber reinforced wood-based epoxy composite (using the resin from liquefied wood without catalyst from both 1.5 h and 5 h liquefaction, ratio of resorcinol to wood: 1).

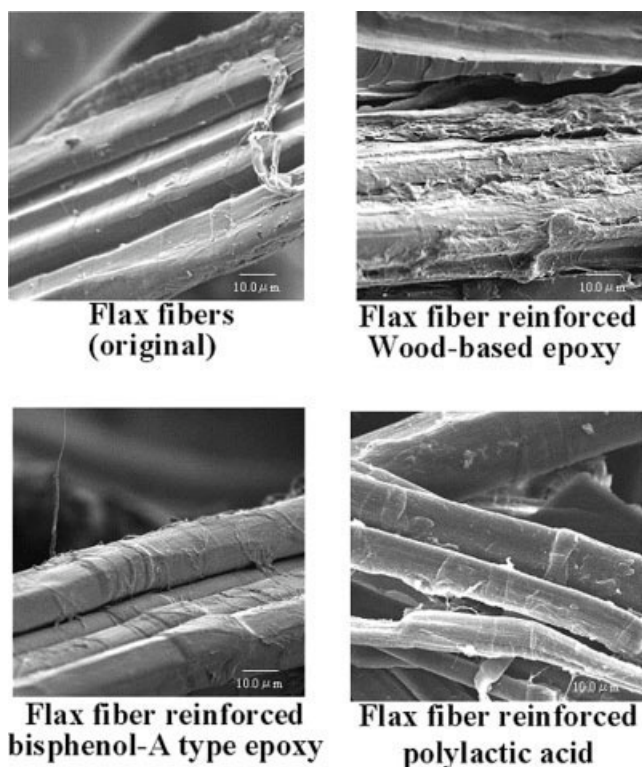


Figure 14 Scanning electron micrographs of the fractured surfaces of the cured flax-fiber reinforced composites (matrix resin: wood-based epoxy, bisphenol A type epoxy, and polylactic acid) and the surface of the original flax fibers.

fibers. This indicates the superiority of the wood-based epoxy resins in terms of adhesive properties.

CONCLUSIONS

Wood-based epoxy resins were newly synthesized from resorcinol-liquefied wood biomass. The modulus of elasticity and the strength of the cured wood-based epoxy resin were equivalent to those of the bisphenol A type epoxy resin at room temperature.

The epoxy functionality of the wood-based resins was controlled by the concentration of phenolic OH groups in the liquefied wood, which would be a dominant factor for the crosslink density and the properties of the cured epoxy resins.

The wood-based epoxy resins indicated good adhesive property to plywood and flax fibers. The high modulus of elasticity and the good adhesive property of the wood-based epoxy resin indicate their high potential as matrix resins for green composites.

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