Synthesis of Epoxy Resins from Alcohol-Liquefied Wood and the Mechanical Properties of the Cured Resins

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ABSTRACT: New wood-based epoxy resins were synthesized from alcohol-liquefied wood. Wood was first liquefied by the reaction with polyethylene glycol and glycerin. The alcohol-liquefied wood with plenty of hydroxyl groups were precursors for synthesizing the wood-based epoxy resins. Namely, the alcoholic OH groups of the liquefied wood reacted with epichlorohydrin under alkali condition with a phase transfer catalyst, so that the epoxy groups were put in the liquefied wood. The wood-based epoxy resins and the alcohol-based epoxy resins as reference materials were cured with polyamide amine. The glass transition temperature (Tg), the tensile strength, and the modulus of elasticity of the wood-based epoxy resin were higher than those of the alcohol-based epoxy resin. Also, the shear adhesive strength of the wood-based epoxy resin to steel plates was higher than those of the alcohol-based epoxy resins, which was equivalent to the level of petroleum-based bisphenol-A type epoxy resins. The higher Tg of the wood-based epoxy resin than that of the alcohol-based epoxy resin is one of the evidences that the wood-derived molecules were chemically incorporated into the network structures. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 745–751, 2011

Key words: wood; epoxy resins; glass transition temperature; tensile strength; adhesive strength

INTRODUCTION

Plant biomass has attracted attention as a chemical resource for replacing fossil fuel resource, because of the renewability and the carbon neutral nature. Many efforts have been devoted to utilizing the waste biomass as valuable chemical resource for synthesizing polymers. For example, Pu and Shiraishi[1–3] have intensively studied on liquefaction of wood biomass. Wood can be decomposed and liquefied by reaction with phenols or alcohols. The liquefied wood has high reactivity because of the large amount of phenolic OH groups and alcoholic OH groups. Using the functionality, phenolic resins and polyurethane forms were synthesized from the liquefied wood.[4–10] The liquefied wood has more potentiality as a resource for other valuable biomass-based resin families.

Epoxy resins have good mechanical and adhesive performances, and therefore, they are widely used in various fields, such as adhesives, coating resins, and matrix resins of composites. We have already synthesized wood-based epoxy resins from the liquefied wood with a kind of phenols (resorcinol).[11,12] The resorcinol-liquefied wood-based epoxy resin indicated the good adhesiveness and the mechanical properties for the matrix resins of fiber-reinforced composites. However, in view of environmental safety, alcohols would be better chemicals than phenols as the liquefaction solvents.

The objectives of this study are to synthesize new wood-based epoxy resins from the alcohol-liquefied wood and to evaluate the mechanical properties and adhesive properties of the cured wood-based epoxy resins.

EXPERIMENTAL

Materials

Wood powder from German spruce (Picea abies) was used as a raw material. The powder sizes were controlled from 20 to 80 meshes. Polyethylene glycols (PEG; PEG400, PEG200, and ethylene glycol) and glycerin as alcoholic solvents and a sulfuric acid as a catalyst were used as chemicals for the liquefaction of wood. Epichlorohydrin, sodium hydroxide (NaOH), and tetrabutylammonium hydrogen sulfate (TBAHS) were used for the synthesis of epoxy resins. All chemicals were reagent grade and were used without further purification. The resins were cured

with a stoichiometric amount of polyamide amine (PAA; active hydrogen equivalent: 63 g/eq produced by Fuji Chemicals, Japan).

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. First, wood powders were liquefied by the reaction with alcohols (mixture of PEG: PEG400 and glycerin, PEG/glycerin = 8/2 in weight ratio). In detail, the wood was liquefied by a reaction with alcohols, and a small amount of sulfuric acid was used as a catalyst (alcohols : sulfuric acid = 100 : 3 in weight ratio) in a glass flask at 140°C. The alcohol/wood weight ratio was 2, and the liquefaction time changed (the standard liquefaction time was determined as 90 min). To quantify the insoluble residue, the black liquid after the liquefied treatment was diluted to 24-fold by one, 4-dioxane/water (4/1 in weight ratio), and filtered with a glass-fiber paper (Toyo GA-100: 1 μm particle-retainable). After drying in an oven at 100°C, the dioxane-insoluble residue was weighed. The amounts of the residue were expressed as weight percents on the basis of the wood samples. The reason of using the glycerin with PEG as a component of wood-liquefaction solvents was to reduce the insoluble residue in the liquefaction process and to increase the amount of the biomass components in the liquefied wood.[13]

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. Firstly, the liquefied wood and epichlorohydrin were put into a glass flask. The amount of epichlorohydrin was set as the molar ratio of epichlorohydrin/alcoholic OH in the liquefied wood was 15. This means the epichlorohydrin was put in the reaction system excessively. After premixing, TBAHS (a phase transfer catalyst) and NaOH (the amount was 4.5-fold in molar ratio compared to alcoholic OH groups) were slowly added to the composition with stirring. The flask was kept at 60°C for 4 h to achieve the addition reaction of epichlorohydrin.

Salts in the reacted products were filtered out with a glass-fiber paper (Toyo GA-100: 1-μm particle retainable). After mixing with distilled water and neutralization in a separating funnel, nonreacted excess epichlorohydrin in the resin solution was evaporated using a rotary evaporator at 90°C under reduced pressure. Then, the wood-based epoxy resins remained in the flask of the evaporator.

Measurement of hydroxyl value of liquefied wood and epoxy equivalent of liquefied wood-based epoxy resins

The hydroxyl value (mg KOH/g) of a liquefied wood was determined according to JIS K1557-1 as the number of milligram of potassium hydroxide equivalent to that of the phthalic anhydride consumed in the phthalification of 1 g of liquefied wood. Also, the epoxy equivalent (g/epoxy group) of synthesized resin was determined according to JIS K7236.

Size exclusion chromatography

The molecular weight distributions of the liquefied wood and the synthesized wood-based epoxy resins were determined using size exclusion chromatography (SEC; PU-2080 HPLC system using JASCO-Borwin-GPC program, JASCO, Japan), equipped with columns, Shodex KF-801 and KF-803. Tetrahydrofuran was used as the solvent. The average molecular weights were calibrated by monodispersed polystyrene standards.

FT-infrared analyses

Infrared (IR) absorption spectra of the samples were measured using an FT-IR 4100 spectrometer (JASCO) by the KBr pellet method or the liquid thin layer method.

Curing of resins

To prepare the cured resin specimens, stoichiometric amount of PAA was added as a curing agent into the epoxy resin. Then, the resin compositions were held at 80°C under a vacuum to degas. The resin compositions were poured into preheated silicone-coated molds and cured at 130°C for 4 h and then at 150°C for 2 h. Test specimens were machined from the cured plaques with a thickness of 2 mm.

Dynamic mechanical analyses

The temperature dependencies of the viscoelastic properties (storage modulus: E′, loss modulus: E″, and mechanical loss tangent: tanδ) of the cured resins were evaluated by dynamic mechanical analyses in the bending mode using a dynamic frequency of 1 Hz. The instrument used was a DMS6100 (Seiko Instruments). Cured resin specimens with a length of 45 mm, a width of 10 mm, and a thickness of 2 mm were machined from 2-mm thick cured plaques. The samples were tested over a temperature range between −100 and 150°C in the heating rate of 2°C/min. The glass transition temperatures (Tg) and rubbery plateau values of the storage modulus (Er′) were determined. Tg was defined as the peak temperature of the tanδ. From the Er′, the molecular weight between crosslinks (Mc) of the cured resin was calculated using the following Eq. (1)
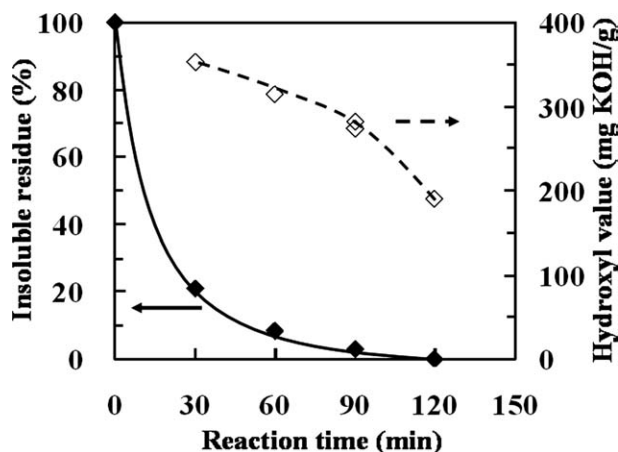
Figure 1 Insoluble residue (% w/w) after the PEG400/glycerin liquefaction of wood and hydroxyl values of the PEG400/glycerin-liquefied wood, in relation to the reaction time for the liquefaction.

$$Mc = 3\varphi\rho RT/Er' \qquad (1)$$

with $\varphi = 1.0$ as a front factor, and $\rho = 1.2$ g/cm^3 as a density of cured resins. R is a gas constant, and T is the absolute temperature of Tg + 40 K.[14–16]

Tensile tests for cured resins

Rectangular specimens with a gauge length of 25 mm, a total length of 40 mm, a width of 5 mm, and a thickness of 2mm were machined from the 2-mm thick cured plaques. Mechanical properties of the cured resin specimens were evaluated in the tensile mode using the testing machine "INTESCO" with a crosshead speed of 10 mm/min at 23°C.

Shear adhesive strength

The steel plates with a length of 125 mm, a width of 25 mm, and a thickness of 1.5 mm were used as the substrates for adhesive tests. The steel plates had been wiped with acetone to clean the surfaces before bonding. Epoxy resins were applied to the substrates and then brought into contact. The length of the lap joint was 10 mm. The bonded specimens were cured at 130°C for 4 h and then at 150°C for 2 h, with pressure of 140 kPa to the specimens. The tensile shear adhesive strength of the specimens was evaluated using the testing machine "INTESCO" in accordance with JIS K 6850 at a crosshead speed of 10 mm/min at 23°C.

RESULTS

Synthesis of wood-based epoxy resins

Wood powder was liquefied by the reaction with alcohols (mixture of PEG400 and glycerin, PEG/glycerin = 8/2 in weight ratio) at 140°C. Figure 1 shows the relationships between the amount of the insoluble residue after the liquefaction or the hydroxyl values of the liquefied wood and the reaction time for the wood liquefaction. The amount of the insoluble residue decreased with increasing the reaction time. The 90-min reaction resulted in almost no insoluble residue.

According to the existing studies, the components of wood are decomposed in the early stage of the liquefaction reaction with alcohols under acid condition.[17–19] In case of liquefaction with monoalcohols, the cellulose was degraded and produced alkyl glucosides, alkoxymethyl furfurals (alcohol ethers of hydroxymethylfurfural [HMF]), alkyl levulinates, and alkyl formates.[17] In case of liquefaction using polyhydric alcohols such as PEG, cellulose is degraded and produces PEG-glucosides, first. If the liquefaction reaction is prolonged, the PEG-glucosides are decomposed to HMF derivatives as intermediates. The HMF derivatives are further decomposed to produce levulinic acid PEG esters.[18] Meanwhile, the HMF derivatives become the source of the condensed insoluble residue.[17] However, the addition of glycerin has a role to prevent the recondensation of decomposed wood components and decreases the insoluble residue.[13,18]

It should be noted that plenty of hydroxyl groups remain in the liquefied wood, as shown in Figure 1. Namely, the liquefied wood can be the precursor of the wood-based epoxy resin. Meanwhile, the hydroxyl values decreased with increasing the reaction time. This would mean that the hydroxyl groups were capped or decomposed in the liquefaction processes. From the balance of both the hydroxyl value of the liquefied wood and the insoluble residue, the standard liquefaction time was determined as 90 min.

Next, wood-based epoxy resins were synthesized using the procedure as described in the synthesis of wood-based epoxy resins. Figure 2 shows the reaction routes for glycidyl etherification (epoxidation) of alcoholic OH groups with NaOH and TBAHS as a phase transfer catalyst.[20] The synthesized resin was in a liquid state at room temperature, which was desirable for use as an adhesive resin.
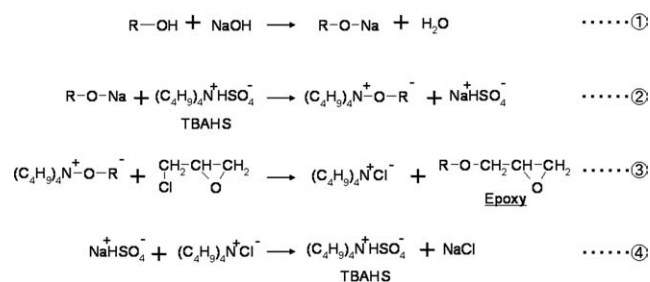

Figure 2 Reaction routes for glycidyl etherification (epoxidation) of alcoholic OH groups using NaOH and TBAHS.
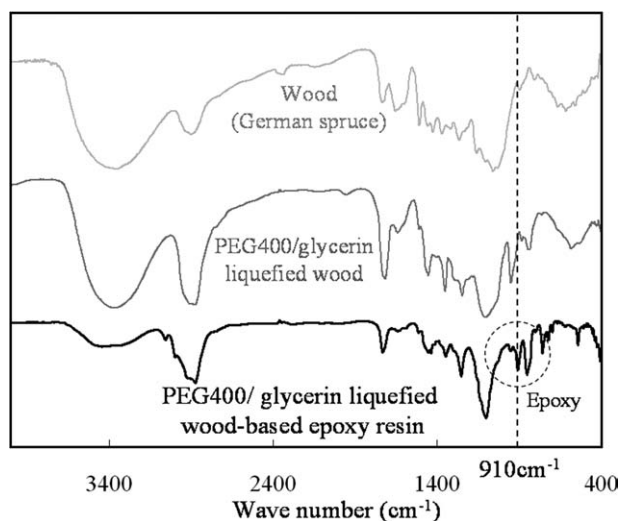
Figure 3 IR spectra of wood powder, PEG400/glycerin-liquefied wood, (alcohol/wood = 2, liquefaction at 140°C in 90 minute) and the PEG400/glycerin-liquefied wood-based resin.

Figure 3 shows the IR spectra of the wood powder, the PEG400/glycerin-liquefied wood, and the liquefied wood-based resin. The IR absorption at 910 cm^{-1} in the spectra shows the vibration of the epoxy groups. This indicates that the liquefied wood-based resin includes epoxy functionality.

Figure 4 shows the SEC of the liquefied wood and also shows the resin synthesized from the liquefied wood. The number of average molecular weights of the liquefied wood was about 700 by polystyrene standards calibration. This means that the polymeric wood components, cellulose, hemicellulose, and lignin, decomposed to a great extent during the liquefaction reaction. The depolymerization transformed the solid-state wood into the liquid-state material. It
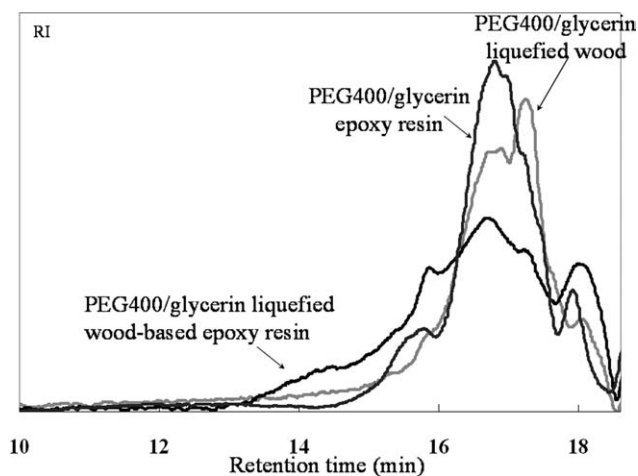

Figure 4 SEC for the PEG400/glycerin-liquefied wood and the synthesized resin from the liquefied wood (alcohol/wood = 2, liquefaction at 140°C in 90 min) and that of glycidyl ether of PEG400/glycerin as a reference material.

should be noted that the distribution of retention time of the wood-based resin synthesized from the liquefied wood and epichlorohydrin was earlier than that of the liquefied wood. The molecular weights of the wood-based resin were about 740 by polystyrene standards calibration. This means that the molecular weights of the liquefied wood increased by the reaction with epichlorohydrin.

Also, the epoxy equivalent of the wood-based resin was determined as 150 g/eq by the titration method described in the measurement of hydroxyl value of liquefied wood and epoxy equivalent of liquefied wood-based epoxy resins. The epoxy equivalent of the corresponding alcohol-based epoxy resin (PEG400/glycerin glycidyl ether) was 245 g/eq, which was quite different from the wood-based epoxy resin. This suggests that the wood-derived molecules were incorporated into the synthesized epoxy resin by chemical reaction.

All the data of the IR spectra in Figure 4, the SEC in Figure 5, and the epoxy equivalent by the titration
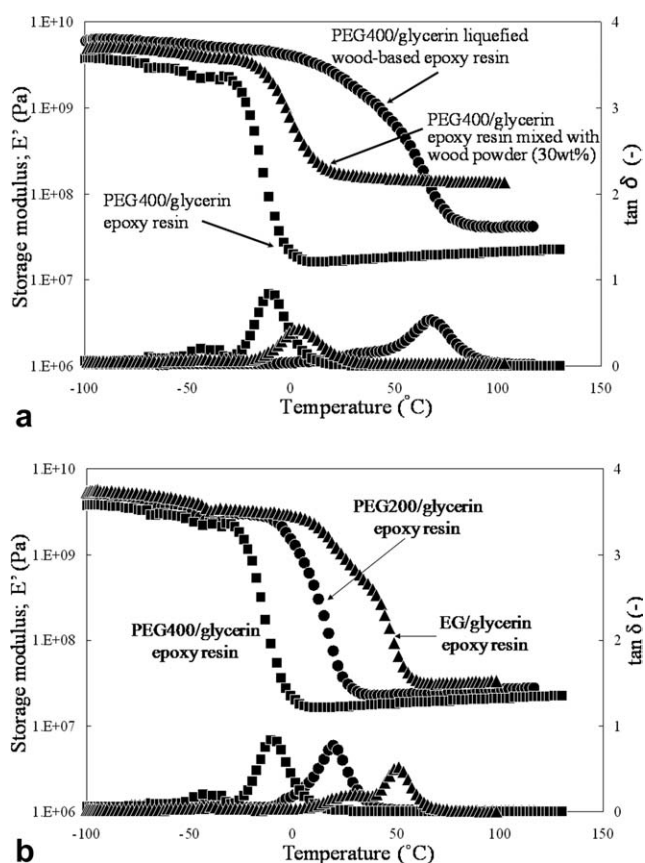

Figure 5 (a) Dynamic viscoelastic properties of the PEG400/glycerin-liquefied wood-based epoxy resins: ●, PEG400/glycerin glycidyl ether: ■, and PEG400/glycerin glycidyl ether mixed with wood powder (30 wt %): ▲. (b) Dynamic viscoelastic properties of the PEG400/glycerin glycidyl ether: ■, PEG200/glycerin glycidyl ether: ●, and EG/glycerin glycidyl ether: ▲. All resins were cured with stoichiometric amount of PAA.
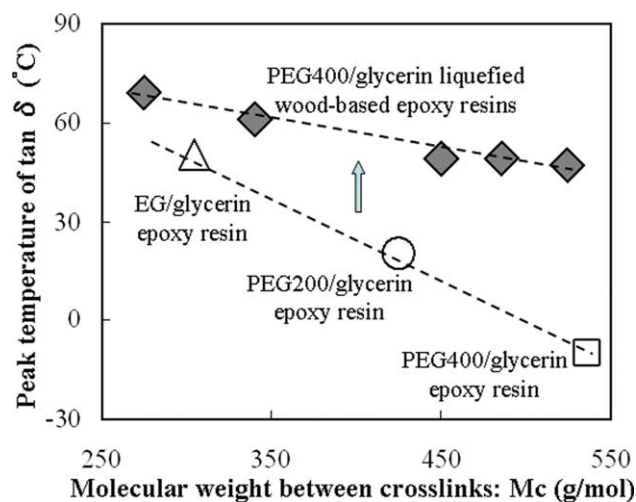
Figure 6 Relationship between molecular weight between crosslinks (Mc) and Tg (peak temperature of tan δ). PEG400/glycerin-liquefied wood-based epoxy resin: ◆, PEG400/glycerin glycidyl ether: □, PEG200/glycerin glycidyl ether: ○, and EG/glycerin glycidyl ether: △. All resins were cured with stoichiometric amount of PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

show that the glycidyl etherification of the OH groups of alcohol-liquefied wood was achieved and the wood-based epoxy resins were synthesized.

Viscoelastic properties of cured wood-based epoxy resins

Figure 5 shows the dynamic viscoelastic properties of the cured epoxy resins. Three epoxy resins, namely, the PEG400/glycerin-liquefied wood-based epoxy resin (the biomass content was 25 wt % in the cured resin), PEG400/glycerin epoxy resin, and PEG400/glycerin epoxy resin physically mixed with 30 wt % of wood powders are compared in Figure 5(a). All resins were cured with stoichiometric amount of PAA. The wood-based epoxy resin had high stiffness in the glass state and had a clear rubbery plateau region after the Tg. This means that the network structure was formed by crosslink reaction between the resin and the curing agent. Also, the wood-based epoxy resin had much higher stiffness and higher Tg than the PEG400/glycerin epoxy resin (the reference material).

In general, the rubbery plateau value of the storage modulus (Er′) has strong relation to the average crosslink density of the cured resins.[14–16] Figure 5(b) shows the dynamic viscoelastic properties of three resins, namely, PEG400/glycerin epoxy resin, PEG200/glycerin epoxy resin, and ethylene glycol/glycerin epoxy resin, which were cured by stoichiometric amount of PAA. The molecular weights between crosslinks (Mc) of the cured resins were calculated from the Er′ using the Eq. (1).

The calculated Mc of the PEG400/glycerin-liquefied wood-based epoxy resin was 260, and the Mc of

the corresponding alcohol-based epoxy resin (PEG400/glycerin glycidyl ether) was 535. Namely, the wood-based epoxy resin had higher crosslink density than the corresponding alcohol-based epoxy resin. The Mc of the wood-based epoxy resin was less than 2-fold of the epoxy equivalent of the epoxy resin (150 g/eq). This suggests that the wood-based epoxy is more than bifunctional. Then, the relationships between the Mc and the Tg of the cured resins were examined in Figure 6. In the three types of PEG/glycerin epoxy resins, the Tg shows the clear relation to the Mc. Meanwhile, the PEG400/glycerin-liquefied wood-based epoxy resin had higher Tg than the PEG/glycerin epoxy resins at the same Mc. In general, Tgs of epoxy resins are determined from both Mc and the chemical structures between crosslink points. Although the high crosslink density (the small Mc) of the wood-based epoxy resin is one reason of the high Tg, the other reason of the high Tg would be relatively rigid chemical structures of the wood-derived molecules between crosslink points.

Moreover, the broad relaxation around the Tg of the wood-based epoxy resin suggests the diversity of crosslink structures in the cured resin. It should be noted that the cured resin of PEG400/glycerin epoxy resin physically mixed with 30 wt % of wood powders did not have the broad relaxation, and the Tg was nearly equal to that of PEG400/glycerin epoxy resin. The broad relaxation is the other evidence that the wood-derived molecules with various structures were chemically incorporated into the network structures.

Tensile properties of cured wood-based epoxy resins

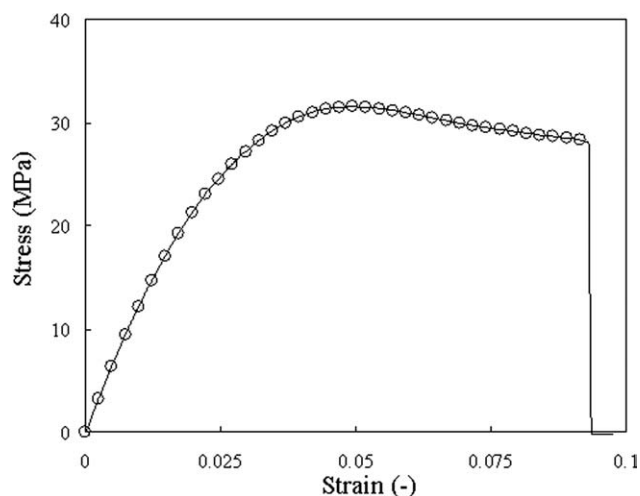Figure 7 shows the tensile properties (the stress-strain behaviors) of the PAA-cured PEG400/

Figure 7 Tensile properties (stress-strain behaviors) of the PAA-cured PEG400/glycerin-liquefied wood-based epoxy resins at 23°C.

TABLE I
Tensile Properties and Lap-Shear Adhesive Strength of the PEG400/Glycerin
Liquefied Wood-Based Epoxy Resin, in Comparison with Those of the
PEG400/Glycerin Epoxy Resin, the PEG200 Epoxy Resin and Bisphenol-A
Type Epoxy Resin at 23°C

	PEG400/glycerin liquefied wood-based epoxy resin	PEG400/ glycerin epoxy resin	PEG200 epoxy resin	Bisphenol-A type epoxy resin
Tensile strength (MPa)	27.9	1.4	3.5	62.8
Yield stress (MPa)	31.6	–	–	–
Tensile modulus (GPa)	1.27	0.04	0.01	2.06
Lap-shear adhesive strength (MPa)	14.5	1.5	1.7	14.6

All resins were cured with PAA. Adhesive substrates were steel plates.

glycerin-liquefied wood-based epoxy resins at 23°C. The PEG400/glycerin-liquefied wood-based epoxy resin has much higher strength and modulus of elasticity than PEG-based cured epoxy resins without wood components (Table I). The PEG400/glycerin-liquefied wood-based epoxy resin is in the glass state at 23°C, as shown in Figure 5. Meanwhile, the PEG400/glycerin epoxy resin is in rubbery state. This is the main reason to explain the big difference of stress-strain behaviors.

Adhesive properties of wood-based epoxy resins

Figure 8 shows the comparison of the lap shear adhesive strengths of the epoxy resins at 23°C. The shear adhesive strength of the wood-based epoxy resin was much higher than that of the PEG400/glycerin epoxy resin. Many hydroxyl groups produced by the reaction between epoxies and amines would increase the adhesive strength of the wood-based epoxy to steel plates having oxidized surfaces.
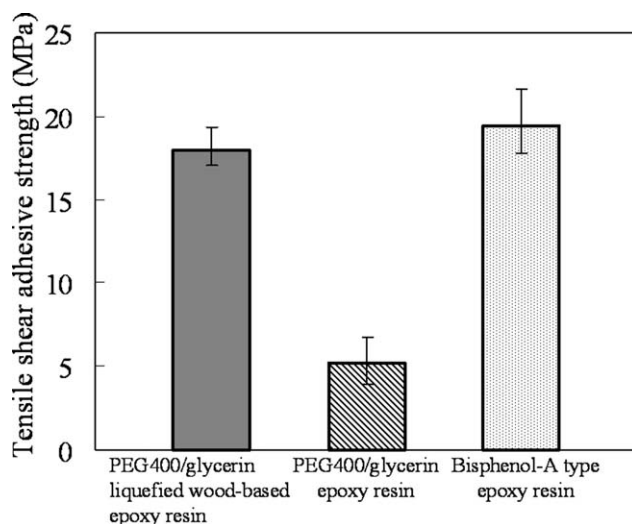

Figure 8 Lap-shear adhesive strengths of the PAA-cured PEG400/glycerin liquefied wood-based epoxy resins, in comparison to PEG400/glycerin glycidyl ether and bisphenol-A type epoxy resin at 23 C. Adhesive substrates: steel.

The fracture occurred mainly in cohesive failure mode of the wood-based epoxy adhesive resins. Therefore, the mechanical properties of the wood-based epoxy resins would be the dominant factors to determine the adhesive strength. Moreover, the adhesive strength of the wood-based epoxy resin was equivalent to that of the petroleum-based bisphenol-A type epoxy resin. In case of bisphenol-A type epoxy adhesives, the fracture occurred mainly not in cohesive failure mode but in the interfacial failure mode (between the resin and the steel plate). The mechanical strength itself of the bisphenol-A type epoxy resin (70 MPa) was higher than that of the wood-based epoxy (32 MPa), but the mechanical strength of the bisphenol-A type epoxy resin would not work on the adhesive strength in the interfacial failure mode. The interfacial strength between the resin and the steel plates would be the key factor to determine the adhesive strength.

CONCLUSIONS

1. Wood-based epoxy resins were newly synthesized from alcohol-liquefied wood biomass. Alcoholic OH groups of the liquefied wood reacted with epichlorohydrin under alkali condition with a phase transfer catalyst, and the epoxy functionality was introduced to the liquefied wood.
2. The Tg, the tensile strength, and the modulus of elasticity of the wood-based epoxy resin cured with PAA were higher than those of the corresponding PEG-based epoxy resin. Also, the shear adhesive strength of the wood-based epoxy resin to steel plates was higher than the PEG-based epoxy resin, and the adhesive strength was equivalent to the level of petroleum-based bisphenol-A type epoxy resins.
3. The high Tg and the broad relaxation around the Tg of the wood-based epoxy resin are evidences that the wood-derived molecules were chemically incorporated into the network structures.

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