WOOD-BASED EPOXY RESINS AND THE RAMIE FIBER REINFORCED COMPOSITES

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Abstract

Wood-based epoxy resin was synthesized from resorcinol-liquefied wood. First, wood components were depolymerized and liquefied by reaction with resorcinol. The resorcinol-liquefied wood with plenty of hydroxyl groups could be considered as a precursor for synthesizing wood-based epoxy resin. Namely, the phenolic-OH groups of the liquefied wood reacted with epichlorohydrine under alkali condition. By the glycidyl etherification, epoxy functionality was introduced to the liquefied wood. The wood-based epoxy resin was cured with 4, 4'- diamino diphenyl sulphone (DDS) and the thermal and mechanical properties were evaluated. The flexural modulus and strength of the cured wood-based epoxy resin were comparable to those of the petroleum-based bisphenol-A type epoxy resin (diglycidyl ether of bisphenol-A: DGEBA). The mechanical and adhesive properties of the wood-based epoxy resins suited well for matrix resins of fiber reinforced composites. Therefore, biomass composites consist of ramie fibers and the wood-based epoxy resin were fabricated. The flexural modulus and strength of the biomass composites were equivalent to those of the same fiber reinforced bisphenol-A type epoxy composites.

Keywords: biomass, composites, fibers, modulus, resins, strength

1. Introduction

It is essential that industrial systems respect anti-global warming restriction. An effective use of plant biomass should be an ideal replacement for fossil fuel resource. 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 had been intensively studied by Lin et al. (1994, 1997), Pu and Shiraishi (1993a, 1993b, 1994), Yao et al., (1993). The 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 could be converted to phenolic resins and polyurethane forms (Lin et al., 1995a, 1995b; Maldas and Shiraishi, 1996; Yao et al., 1995). Liquefied wood would have 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, such as adhesives, coatings and matrix resins of composites. The first objective of this study is to synthesize wood-based epoxy resins using the liquefied wood as the precursor of the resin. The second objective is to fabricate biomass composites consist of the wood-based epoxy as matrix resin and plant fibers as reinforcements, and to evaluate the mechanical properties.

2. Experimental

2.1. Materials

The wood sample used was 20-80 mesh powder from German spruce (*Picea abies*). Resorcinol, epichlorohydrine, and all other chemicals for liquefaction of wood and synthesis of wood-based epoxy resins were of reagent grade and were used without further purification.

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A mixture of diglycidyl ether of bisphenol-A oligomers (Ep828:Ep1001=7:3 in mass ratio, produced by Japan Epoxy Resin Inc.) was used as a reference epoxy resin. The epoxy resins were cured with a stoichiometric amount of 4,4'-diamino diphenyl sulphone (DDS).

2.2. Synthesis of wood-based epoxy resins

2.2.1 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.

The wood was liquefied with resorcinol at 250°C in a pressure-proof reaction tube (TVS-1 type, Taiatsu Glass Industry Inc.) made of SUS-316 stainless steel (Pu and Shiraishi,1993a, b). The resorcinol / wood ratio was 1.

In order to quantify the insoluble residue in the liquefaction process, 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: 1μm particle-retainable). After drying in an oven at 80°C, the dioxane-insoluble residue was weighed. The amounts of the residue are expressed as mass percents on the basis of the wood samples used.

The hydroxyl value of the liquefied wood is defined as the amount (milligrams) of potassium hydroxide equivalent to the acetic anhydride consumed in the acetylation of 1 g of liquefied wood sample and was determined according to JIS K0070.

2.2.2 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 with phenolic-OH groups and epichlorohydrine were put into a glass flask and the temperature was raised to 100°C while stirring. The amount of epichlorohydrine was set as the molar ratio of epichlorohydrine for resorcinol in the liquefied wood was 10, which means the epichlorohydrine was put in the reaction system excessively. Next, 50 w/w% sodium hydroxide (NaOH) aqueous-solution, corresponding to two times in molar ratio compared to 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 hours in total to achieve the addition reaction of epichlorohydrine and the ring formation of epoxy groups.

The reacted products were diluted ten times with acetone, and salts as by-products were filtered out with a filter paper made of glass-fiber (Toyo GA-100: 1 μm particle-retainable). The acetone and non-reacted excess epichlorohydrine 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.

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

2.3. Gel permeation chromatography

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

2.4. FT-IR analyses

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

2.5. Curing of resins

In order to prepare cured resin specimens, mixtures of epoxy resin and DDS were first heated to 80°C to lower the viscosity of the resin compositions, making it easier for the DDS particles to disperse. Then, the resin compositions were held at 60°C under a vacuum to de-gas. The resin compositions were poured into preheated silicone-coated molds and cured at 130°C for 3 hours then at 140°C for 3 hours. Test specimens were processed from the 2 mm thick cured plaques.

2.6. Dynamic mechanical analyses

The temperature dependencies of the viscoelastic properties (storage modulus: E' and mechanical loss tangent: tanδ) of the cured resins were evaluated by dynamic mechanical analyses (DMA) in the bending mode using a dynamic frequency of 1Hz. The instrument used was a DMS6100 (Seiko Instruments, Inc.). Cured resin specimens with a length of 50 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°C and 180°C with a heating rate of 2°C/minute. The glass transition temperatures (Tg) was defined as the temperature where the tangent line of E' in the glassy region and the tangent line of E' in the transition region intersect.

2.7. Flexural tests for cured resins and composites

The flexural tests for the cured resins and the composites were performed in the three point bending (3PB) mode with a strain rate of 5 mm/min at 25°C.

Specimens with a length of 80 mm, a width of 10 mm, and a thickness of 2 mm were machined from 2mm-thick cured plaques.

2.8. Fabrication of ramie fiber reinforced wood-based epoxy composites

First, uncured resin films composed of mixtures of epoxy resin and DDS were coated on release papers. Additionally, ramie fiber fabrics were cut into 90 mm squares. Each cut fabric was placed between two resin films and pressed to make a fiber / resin prepreg. Next, the prepregs were laid on top of each other and pre-compacted in a nylon-bag sheet under vacuum pressure. The pre-compacted prepregs were placed in a hot-press machine and cured. The curing condition for the composites was at 130°C for 3 hours and 140°C for 3 hours under 10MPa pressure. Test specimens were cut with a diamond saw from the cured composites.

2.9. 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". 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, Japan.

3. Results

3.1. Synthesis of wood-based epoxy resins

Wood powder was liquefied by the reaction with resorcinol. The black, high viscous liquid was considered as a precursor of the wood-based epoxy resin, because the reacted compounds included considerable amount of hydroxyl groups as the reactive sites originated from the wood and the resorcinol.

Fig. 1 shows the relationship between the amount of the insoluble residue and the reaction time for liquefaction. About 1.5 - 2 hours reaction gave the minimum value on the insoluble residue. More than 2 hours reaction resulted in increased insoluble residue, which would indicate that re-condensation of components from degraded wood (polysaccharide and lignin) had occurred (Pu and Shiraishi, 1993a; Yao et al., 1993).

Next, wood-based epoxy resins were synthesized. Fig. 2 shows the synthesized resin after reaction between the liquefied wood (liquefaction time: 1.5 hours) and epichlorohydrine. The resin was in a viscous liquid state at room temperature, which suited for a matrix resin of fiber reinforced composites.

Fig. 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 (Lora and Wayman, 1978; Pu and Shiraishi, 1993a).
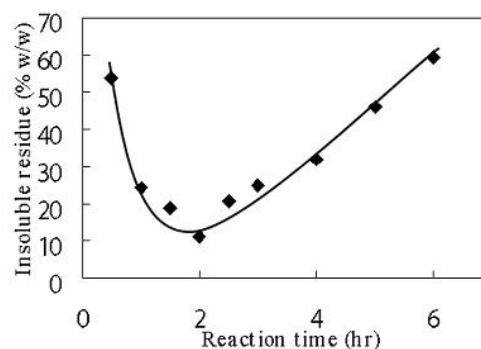

Fig. 1. Insoluble residue (%w/w) generated in the process of liquefaction of wood with resorcinol

Fig. 2. Liquefied wood-based resin after reaction with epichlorohydrine
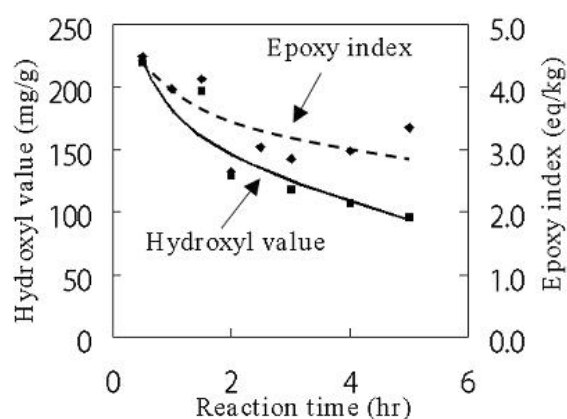

Fig. 3. Relationship between the hydroxyl value of the liquefied wood and the reaction time at 250°C for the wood-liquefaction (resorcinol / wood ratio = 1), and epoxy index of the resin synthesized from the liquefied wood

Fig. 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 depend on the concentration of phenolic-OH groups in liquefied wood as the precursors.

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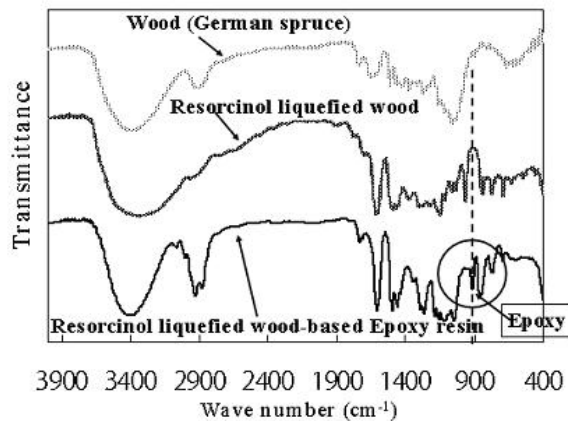

Fig. 4. IR spectra of wood, resorcinol-liquefied wood, and the liquefied wood-based epoxy resin, (liquefaction time = 1.5 hours, resorcinol / wood ratio = 1)

Fig. 5 shows the results of gel permeation chromatography (GPC) for the liquefied wood and for the synthesized resin from the liquefied wood. Namely, the molecular mass of the products, before-and-after the reaction with epichlorohydrine was determined. From the chromatography, the number average molecular mass (Mn) of the liquefied wood was calculated as about 500 by polystyrene standards calibration. This indicated that the polymeric wood components, cellulose, hemicelluloses and lignin, decomposed to a great extent at 250°C. The de-polymerization would have transformed the solid-state wood into the liquid-state material.
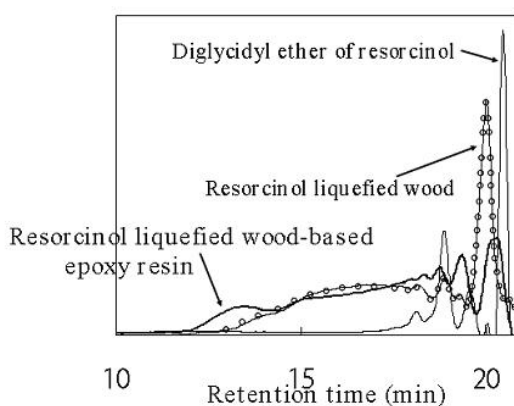

Fig. 5. Gel permeation chromatography (GPC) of the liquefied wood, the synthesized epoxy resin from the liquefied wood, (liquefaction time = 1.5 hours, resorcinol / wood ratio = 1) and that of diglycidyl ether of resorcinol as a reference material

If the liquefied wood reacts with epichlorohydrie, the molecular mass should increase. The distribution of retention time of the synthesized resin was faster than that of the liquefied wood. The Mn of the resin (about 600) became higher than that of the liquefied wood before reaction with epichlorohydrine (about 500). Moreover, the Mn of the resin (about 600) were obviously higher than that of diglycidyl ether of resorcinol (Mn = 390).

All the data of the epoxy index by the titration in Fig. 3, the IR spectra in Fig. 4, and the GPC in Fig. 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.

3.2. Viscoelastic properties of cured wood-based epoxy resins

Fig. 6 shows the dynamic viscoelastic properties of the wood-based epoxy resins cured with DDS. The cured wood-based epoxy resins showed high stiffness at room temperature and a clear rubbery plateau after the Tg. The storage modulus of elasticity of the resorcinol-liquefied wood-based epoxy resin at 25°C was higher than that of the bisphenol-A type epoxy resin. And the rubbery plateau indicates that a crosslink network structure was definitely formed. The Tg of the resorcinol-liquefied wood-based epoxy resin was lower than that of the bisphenol-A type epoxy resin. The broad Tg region would mean there is a diversity of crosslink structures in the cured resin, which suggests that the glycidyl etherified wood components co-reacted, and were incorporated into the crosslink structures.
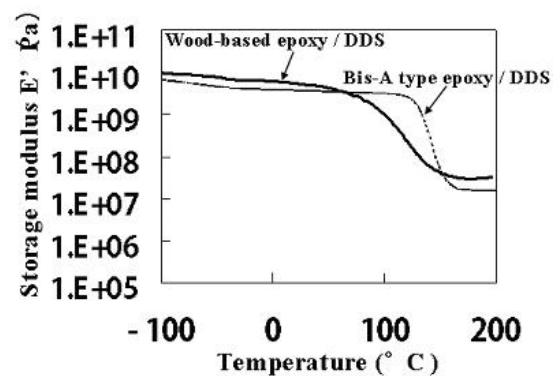

Fig. 6. Dynamic viscoelastic properties of the resorcinol-liquefied wood-based epoxy resin (resorcinol / wood ratio = 1) and the bisphenol-A type epoxy resin (Both were cured with DDS)

3.3. Flexural properties of cured wood-based epoxy resins

Fig. 7 shows the flexural properties (the flexural modulus of elasticity and the flexural strength) of the cured resorcinol-liquefied wood-based epoxy resin at room temperature, in comparison with the bisphenol-A type epoxy resin. The cured wood-based epoxy resin indicated higher flexural

modulus than the petroleum-based bisphenol-A type epoxy resin. The flexural strength of the wood based epoxy resin was almost equivalent to that of the bisphenol-A type epoxy resin. The high stiffness of the wood-based epoxy resin is an attractive property for a matrix resin of fiber reinforced composites.
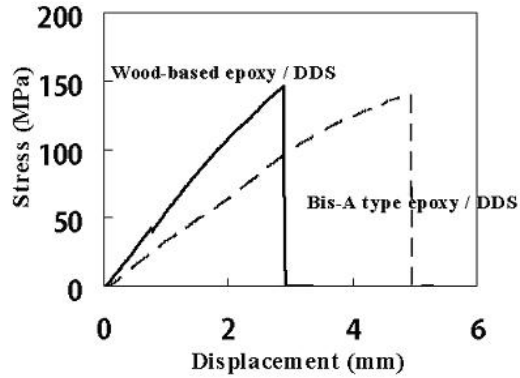

Fig. 7. Flexural stress – displacement behavior of resorcinol-liquefied wood-based epoxy resins and that of the bisphenol-A type epoxy resin. Both were cured with DDS

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

In order to find a suitable application for the wood-based epoxy resin, a natural plant fiber reinforced composites consisting of ramie fibers and the wood-based epoxy matrix resin were fabricated, as shown in Fig. 8. Flexural properties of the ramie fibers reinforced wood-based epoxy composites and the same fiber reinforced bisphenol-A type epoxy composites as reference materials were evaluated, as shown in Fig. 9.

The flexural modulus of elasticity (stiffness) and the strength of composites increased with increasing the content of ramie fibers in both composites (Fig. 9), and the stiffness and the strength of the wood-based epoxy composites were equivalent to those of the bisphenol-A type epoxy composites.

The fracture surfaces of the composites were observed using SEM, as shown in Fig. 10. The observed fiber pull-out phenomenon in the fracture surfaces of the composites is a kind of index of the adhesiveness between the fibers and the matrix resin. Namely, the length of exposed ramie fibers which were pulled out from the fracture surfaces of wood-based epoxy composites was shorter than that of bisphenol-A type epoxy composites.

This suggests that the wood-based epoxy resin has better adhesion to ramie fibers than bisphenol-A type epoxy resin. In the high magnified scale in Fig. 11 also, the surfaces of the ramie fibers were covered well with the wood-based epoxy resin in the composites, and the wood-based resin showed better adhesion to the ramie 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 ramie fibers. That would be one of the reasons to explain the good adhesive property between the wood-based epoxy resin and the biomass fibers.

Fig. 8. Ramie fibers fabric (left) and the ramie fiber reinforced resorcinol-liquefied wood-based epoxy composite (right)
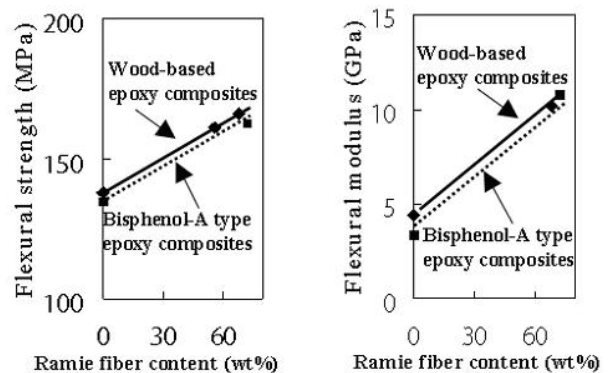

Fig. 9. Flexural strengths and moduli of the biomass composites made from the resorcinol liquefied wood-based epoxy resin and ramie fibers, compared with bisphenol-A type epoxy composites

4. Conclusions

(1) Wood-based epoxy resins were synthesized from resorcinol-liquefied wood biomass.

(2) The DDS cured wood-based epoxy resin indicated higher flexural modulus than the petroleum-based bisphenol-A type epoxy resin at room temperature. The flexural strength of the wood based epoxy resin was almost equivalent to that of the bisphenol-A type epoxy resin.
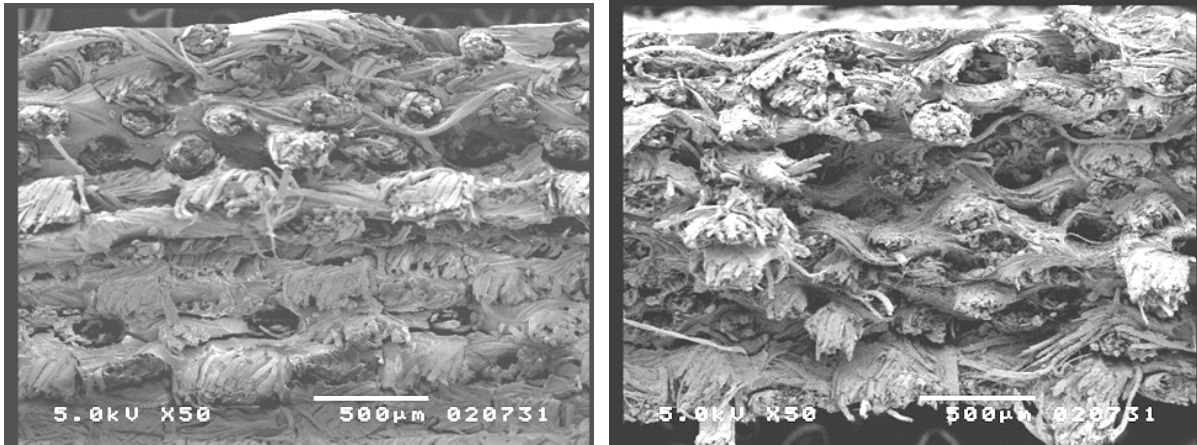
Fig. 10. Scanning electron micrographs of the fractured surfaces of the ramie fiber reinforced epoxy composites (left: resorcinol-liquefied wood-based epoxy composite, right: bisphenol-A type epoxy composite)
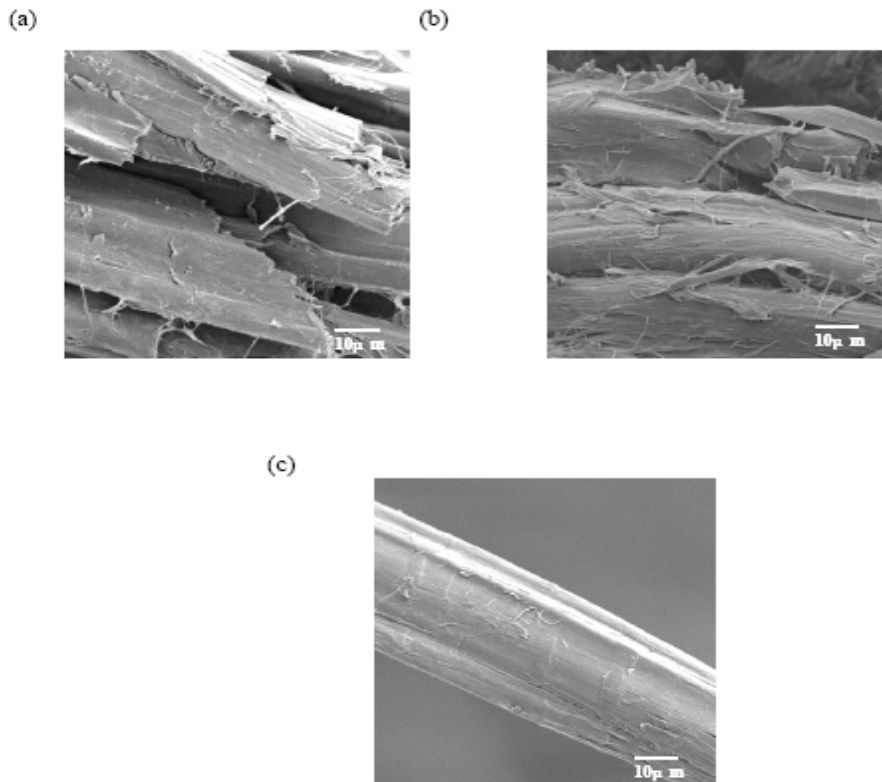

Fig. 11. Scanning electron micrographs of the fractured surfaces of the ramie fiber reinforced epoxy composites: (a) resorcinol-liquefied wood-based epoxy composite, (b) bisphenol-A type epoxy composite, and (c) ramie fiber itself

(3) The wood-based epoxy resins showed good adhesive property to ramie fibers. The high stiffness and the good adhesive property of the wood-based epoxy resin indicate their high potential as matrix resins for biomass-based green composites.

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