

Synthesis and Properties of Copolymer Epoxy Resins Prepared from Copolymerization of Bisphenol A, Epichlorohydrin, and Liquefied *Dendrocalamus latiflorus*

Chiou-Chang Wu, Wen-Jau Lee

Department of Forestry, National Chung-Hsing University, Taichung 402, Taiwan

Received 1 February 2009; accepted 31 October 2009

DOI 10.1002/app.31703

Published online 7 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *Dendrocalamus latiflorus* Munro (ma bamboo) was liquefied in phenol and polyhydric alcohol (polyethylene glycol/glycerol cosolvent) with H₂SO₄ as catalyst. Liquefied bamboos reacted with bisphenol A and epichlorohydrin were then employed to prepare copolymer epoxy resins. The curing property and thermal property of copolymer epoxy resins were investigated. The results showed that copolymer epoxy resins could cure at room temperature after the hardener was added, and its curing process was an exothermic reaction. Comparison showed that copolymer epoxy resins prepared with phenol-liquefied bamboo as raw material had higher heat released than

those prepared with polyhydric alcohol-liquefied bamboo during curing. The DSC analysis showed that heat treatment could enhance the crosslinking of copolymer epoxy resins cured at room temperature. However, resins prepared with polyhydric alcohol-liquefied bamboo had a lower glass transition temperature. The TGA analysis showed that resins prepared with phenol-liquefied bamboo had better thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2065–2073, 2010

Key words: copolymer resin; *Dendrocalamus latiflorus*; epoxy resin; liquefied ma bamboo; thermal property

INTRODUCTION

Fossil resources are extensively employed to manufacture various products used by mankind. However, it is a nonrenewable resource, and its utilization will increase the concentration of CO₂ in air and induce a serious green house effect. Therefore, to find alternative resources is of great need and urgency. Plants constitute biomass materials with a renewable characteristic and are the most plentiful resources on earth. However, the solid nature restricts their application. If we can convert them from solid into liquid, the utilization of plants can substantially be extended.

Solvent liquefaction is one of the ways for converting the biomass from solid into liquid. In general, lignocelluloses those composed of natural polymers, such as cellulose, hemicellulose, and lignin, will be dispersed in the liquefaction solvent with organic or inorganic acid as a catalyst. The chemical components of lignocelluloses will undergo the hydrolysis, degradation, and decomposition reaction under heating. The structure of these polymers will break down to small fragments or monomolecular compounds, followed by reaction with the solvent used

for liquefaction to form derivatives, and then dissolve in the free solvent. The liquefied product can be employed to prepare various synthetic resins depending on the kind of solvent employed. If phenol is used as the solvent, the liquefied product can be employed to prepare phenolic resins. Alma et al.¹ liquefied wood in phenol using HCl as catalyst. The result showed that phenolated wood had thermoflowability, and could be utilized to make moldings when mixed with hexamethylenetetramine and hot-pressed at high temperature. Alma and Basturk² liquefied grapevine cane with phenol using H₂SO₄ as catalyst, and indicated that liquefied grapevine cane could be employed to prepare resol-type phenol-formaldehyde resin (PF) when reacted with formaldehyde under alkaline conditions. Lee et al.^{3,4} used phenolated corn bran to prepare novolak-type PF resins and used phenolated wood to prepare resol-type PF resins. Chen et al.^{5–7} investigated the characteristics of phenol-liquefied moso bamboo, and used the liquefied bamboo to prepare both the resol-type water-soluble and alcohol-soluble PF resins. Lee and Liu⁸ used the liquefied bark to prepare resol-type PF resins, and indicated that these resins could be used in the manufacture of particleboard. Lee et al.^{9,10} used the phenol-liquefied Japanese cedar to prepare the resol-type and novolak-type PF resin, which were then used in the manufacture of plywood and molding, respectively.

Correspondence to: W.-J. Lee (wjlee@dragon.nchu.edu.tw).

TABLE I
Liquefaction Conditions and Properties of Liquefied Bamboo

Liquefaction condition			Properties of liquefied bamboo				
Reagent	Reaction temp. (°C)	Reaction time (min)	Residue content (%)	Nonvolatile (%)	Hydroxyl value	Average molecular weight (M_w)	Polydispersity (M_w/M_n)
Phenol	130	60	2.2	68.9	333.7	759	2.6
Polyol	150	75	5.7	32.8	245.3	2119	3.8

In another liquefaction system, polyhydric alcohol is used as the solvent. The liquefied product can be utilized to prepare polyurethane (PU) resins. Wu and Lee¹¹ investigated the characteristics of polyhydric alcohol-liquefied Japanese cedar and ma bamboo. Kurimoto et al.^{12,13} liquefied Japanese cedar using the cosolvent of polyethylene glycol (PEG)/glycerol, and blended the liquefied wood with polymeric methylene diphenylene diisocyanate (PMDI) to prepare PU films. Lee et al.¹⁴ indicated that liquefied corn bran can be successfully employed to prepare PU foams. Wei et al.¹⁵ investigated the properties and microstructure of PU resins made from liquefied wood. Lee and Chang¹⁶ investigated the effect of the kind of isocyanate on the properties of PU forms made from liquefied wood. Wu et al.¹⁷ investigated the effects of the kind and dosage of surfactants on the properties of PU forms. Lee and Lin¹⁸ liquefied Taiwan acacia and China fir in PEG/glycerol cosolvent, and indicated that liquefied wood when blended with isocyanate could be employed as a PU adhesive.

Epoxy resins contain epoxy groups in its molecular structure. Cured epoxy resins exhibit excellent properties, such as adhesion ability to various substrates, outstanding chemical and corrosion resistance, electrical insulation, mechanical properties, thermal stability, and low shrinkage during curing. In recent years, epoxy resins have been one of the most important polymer materials applied in a broad range of products as adhesives, coatings, moldings, and so on. However, one of the drawbacks of epoxy resins is that they are too expensive. Therefore, researchers investigated the feasibility of using liquefied wood to prepare epoxy resins. Kobayashi et al.^{19,20} used liquefied wood to prepare liquefied wood/epoxy resin. They found that liquefied wood could be incorporated into the resin and formed a crosslinked copolymer network, and they had the shear bonding strength similar to that of the commercial epoxy resin. Asano et al.²¹ liquefied the ozone-treated wood, and then blended the liquefied wood with a neat epoxy resin. They indicated that blended resins could also be used as wood adhesive. Kishi et al.²² prepared a liquefied wood-based epoxy resin, and investigated the mechanical properties and bonding properties of cured resins. In our previous study,²³ the polyhydric alcohol-liquefied wood was blended with epoxy resin and used as a wood adhesive. In this study, both the

phenol- and polyhydric alcohol-liquefied ma bamboo were copolymerized with bisphenol A and epichlorohydrin to prepare copolymer epoxy resins. The curing and thermal properties of cured copolymer resins were investigated.

EXPERIMENTAL

Materials

Dendrocalamus latiflorus Munro (ma bamboo), ~ 5 years old, was felled and collected from Lugu, Nantou, central Taiwan. The bamboo was air-dried and ground to powder with a hammer mill. The bamboo powder with a dimension passing 20 mesh was dehydrated in an oven at 105°C for 24 h before being use. Chemicals such as PEG 400 (Katayama Chemical Co.), glycerol, phenol, and sulfuric acid (Union Chemical Co.) were used for bamboo liquefaction. Bisphenol A (Hayashi Chemical Ind.), epichlorohydrin (Tedia Chemical Co.), and sodium hydroxide (Shimakyu Co.) were used for epoxy resin synthesis. Triethylene tetramine (TETA; Hayashi Chemical Co.) was used as the curing hardener for epoxy resins. All these chemicals were reagent grade and were used without further purification. Tetrahydrofuran (THF; 99.9%; Merck) was HPLC grade, and was used as both solvent and eluant for gel permeation chromatography.

Liquefaction of ma bamboo

To liquefy ma bamboo, 450 g of the phenol or PEG/glycerol cosolvent (9 : 1; w/w) were used as the solvent, which were premixed with 13.5 g of the sulfuric acid (3% according to the weight of solvent) in a 1000-mL separable glass flask equipped with a stirrer, thermometer, and reflux condenser. The solvent was heated to 130°C and 150°C for phenol and polyhydric alcohol, respectively. Then, 150 g of ma bamboo powder was gradually added to the reactor. The weight ratio of liquefaction solvent to ma bamboo was 3/1 (w/w). After all bamboo powder had been added, the liquefaction reaction proceeded under constant heating and stirring for 60 and 75 min for the solvent of phenol and polyhydric alcohol, respectively. Two different liquefied ma bamboos obtained were shown as Table I.

TABLE II
Synthesis Conditions and Properties of Copolymer Epoxy Resins

Resin code	Synthesis conditions		Second stage			Properties of resins		
	First stage		Epichlorohydrin (mol)	Liquefied bamboo		Visc. (cps)	Nonvolatile (%)	EEW ^a
	Epichlorohydrin (mol)	Bisphenol A (mol)		Reagent	Hydroxyl group (mol)			
ER	5	1	–	–	–	3480	90.0	241.3
P-9/1 ^b	4.5	0.9	0.5	Phenol	0.1	8840	93.0	266.5
P-7/3	3.5	0.7	1.5	Phenol	0.3	7080	91.1	264.3
P-5/5	2.5	0.5	2.5	Phenol	0.5	2953	87.3	254.8
O-9/1	4.5	0.9	0.5	Polyol	0.1	6780	91.8	265.0
O-7/3	3.5	0.7	1.5	Polyol	0.3	19780	93.8	366.9
O-5/5	2.5	0.5	2.5	Polyol	0.5	29840	92.1	1173.4

^a EEW: Epoxy equivalent weight.

^b Bisphenol A/liquefied bamboo.

Properties of liquefied ma bamboo

The unliquefied residue was measured by diluting the liquefied bamboo with methanol, followed by filtering through a G3 glass filter in a vacuum. The residue was dried in an oven at 103°C, and calculated according to the weight of bamboo used. The nonvolatile content was measured by heating the liquefied bamboo at 180°C to remove unreacted solvent and calculated using the weight of nonvolatile matter. The hydroxyl value was measured by the method described in our previous article.¹⁸ The pyridine/acetic anhydride mixture (7/3; v/v) was charged into the liquefied bamboo, and heated at reflux temperature for 20 min. After cooling, 25 mL of toluene and 50 mL of water were added, followed by titration with 1N KOH_(aq). The change in pH was monitored with a pH meter, and the neutralization volume was obtained from the neutralization curve.

Synthesis of liquefied bamboo-bisphenol A copolymer epoxy resins

Copolymer epoxy resins were synthesized by a two-step process as shown in Table II. The total amount of epichlorohydrin used was 5 mol. In the first step, the mixture of epichlorohydrin and bisphenol A with a molar ratio of 5/1 as shown in Table II was charged into a four-necked glass reaction flask, and the reaction took place at 110°C for 2 h under a continuous stirring and dripping of NaOH_(aq). Then, other epichlorohydrin (0.5, 1.5, and 2.5 mol) and calculated amount of liquefied bamboo (0.1, 0.3, and 0.5 mol hydroxyl group) were added. Copolymerization proceeded under continuous dripping of the remaining NaOH_(aq) during a period of 2 h at the same temperature. The total amount of NaOH added was 1 mol. Finally, the reaction was continued for another 1 h and cooled to room temperature.

The byproduct of NaCl was removed by filtration, whereas the water and unreacted epichlorohydrin were removed by reduced pressure distillation.

Characterization of copolymer epoxy resins

The nonvolatile matter was measured by drying resins in an oven at 135°C for 60 min. The viscosity was measured by a Brookfield viscometer at 25°C. The epoxy equivalent weight (EEW) was measured by putting 0.5–1.0 g of resins into a 250-mL Erlenmeyer flask, followed by adding 25 mL of 0.2N HCl-pyridine solution. The sample was heated at reflux temperature for 20 min, and then cooled to room temperature. Then, 50 mL of toluene were added and titrated with the solution of 0.5N NaOH-methanol. The change in pH was monitored with a pH meter, and the neutralization volume was obtained from the neutralization curve. The EEW was calculated by the following equation: $EEW = (1000 \times W) / [N \times (B - S)]$, where B and S are the volume (mL) of NaOH solution consumed for the blank and sample test, respectively, N is the normality of the NaOH solution, and W is the weight (g) of the sample.

GPC molecular weight analysis

The molecular weight and molecular weight distribution of liquefied bamboo and copolymer epoxy resins were measured by gel permeation chromatograph (GPC; Hitachi L-6200A) equipped with Shodex KF-802 column, and monitored with a UV detector. THF was used as the solvent and eluant. The concentration of sample was 0.1%, and filtrated with a 0.45- μ m filter film. The flowing rate and injection volume were 1 mL/min and 15 μ L, respectively. The monodisperse polystyrene was used as the standard.

Curing test of copolymer epoxy resins

For curing test, an equivalent weight of epoxy resin and TETA, from the epoxy group and amino group, respectively, was mixed and stirred continuously until cured. The variations in temperature during curing were monitored using an electronic thermometer. When completely set, the block resin was ground into powder and immersed in acetone for 24 h, followed by filtrating and drying. The weight retention percentage was employed to indicate the gel degree of the cured resin.

DSC thermoanalysis of copolymer epoxy resins

The DSC thermoanalysis was carried out by a differential scanning calorimeter (Perkin-Elmer DSC-7) with a three-stage scanning method. In the first stage, the heat flow of resin mixed with TETA was detected using an isothermal program at 30°C for 4 h. Then, thermal scanning from 30 to 200°C at a heating rate of 10°C/min was carried out. Finally, the same thermal scanning process was conducted once again.

TGA thermoanalysis of cured resins

A thermal gravimetric analyzer (Perkin-Elmer Pyris 1 TGA-7) was employed to measure the thermal degradation of cured resins. About 7–10 mg of resin powder was put into the sample pan, and the degradation reaction was conducted under a nitrogen atmosphere by increasing the temperature from 50 to 800°C at a heating rate of 10°C/min.

RESULT AND DISCUSSION

Properties of liquefied ma bamboo

Ma bamboo was liquefied using phenol and polyhydric alcohol as solvents in this study. Yamada and Ono²⁴ liquefied wood and cellulose using ethylene carbonate or propylene carbonate as solvents. They indicated that cellulose would degrade to levulinic acid followed by combination with the solvent to form derivatives. Lin et al.²⁵ used the guaiacylglycerol- β -guaiacyl ether (GG) as a model compound of lignin to investigate the liquefaction mechanism in phenol. They indicated that the dominant reaction pathways included a condensation between phenol and GG in its C- α , and further cleavages at both β -O-4 linkage and C $_{\beta}$ -C $_{\gamma}$ bonding. The main products included guaiacol, triphenylethanes, diphenylmethanes, benzocyclobutanes, and phenylcoumarans. In addition, Lin et al.²⁶ used the cellobiose as a model compound to study the liquefaction mechanism of cellulose. They indicated the oxygen atoms at both the glycosidic bonds and C-1 hydroxy of reducing

end group were initially protonated, followed by cleavage of the glycosidic bond and formed carbonium ions. These carbonium ions would react with phenol through nucleophilic substitution to produce phenolated compounds.

As shown in Table I, ma bamboo that was liquefied with phenol and polyhydric alcohol as solvent had residue contents of 2.2 and 5.7%, respectively. It means that most of lignocellulosic materials had degraded and decomposed to lower molecular component, and reacted with liquefaction solvents to form derivatives. This conversion led them having a better compatibility with the solvent, and dissolved in the free solvent to form a liquid solution. However, some of the residues were still existing, which includes unliquefied bamboo and recondensed products during liquefaction.²⁷

The nonvolatile matter is the component that cannot be removed as the liquefied bamboo was heated at 180°C. It includes degraded and decomposed lignocelluloses, derivatives, and residues. They were 68.9% and 32.8% for phenol- and polyhydric alcohol-liquefied bamboo, respectively. Because both of the liquefied bamboo had the same weight ratio of bamboo to solvent at the initial stage of liquefaction, the higher nonvolatile of the phenol-liquefied bamboo means it had more amount of derivative that formed by the combination of bamboo with phenol.

The hydroxyl value, which is expressed as mg of KOH/g, indicates the OH groups that are present in the liquefied bamboo.^{28,29} They were 333.7 and 245.3 for phenol- and polyhydric alcohol-liquefied bamboo, respectively. For the polyhydric alcohol-liquefied bamboo, degraded or decomposed ingredients would react with the solvent by the etherification, a reaction between the OH group of bamboo components and solvents, and would decrease the hydroxyl value of the liquefied bamboo. For the phenol-liquefied bamboo, the degraded or decomposed components of bamboo would react with phenol by a *para*- and *ortho*-substitution to form hydroxyl benzene derivatives. It will retain the OH group of the phenol and will keep the functionality of phenol in the derivatives.³⁰

The result that ma bamboo liquefied with phenol as solvent had less residue, more nonvolatile matter, and higher hydroxyl value suggests that ma bamboo liquefied using phenol as solvent had better effect than that using polyhydric alcohol as solvent.

Moreover, as shown in Table I, ma bamboo liquefied with phenol as solvent had lower weight-average molecular weight and smaller molecular weight polydispersity than that liquefied with polyhydric alcohol as solvent. Figure 1 shows that the molecular weight distribution of the liquefied bamboo was distinguished into two regions. The low-molecular-weight region was attributed to the free solvent,

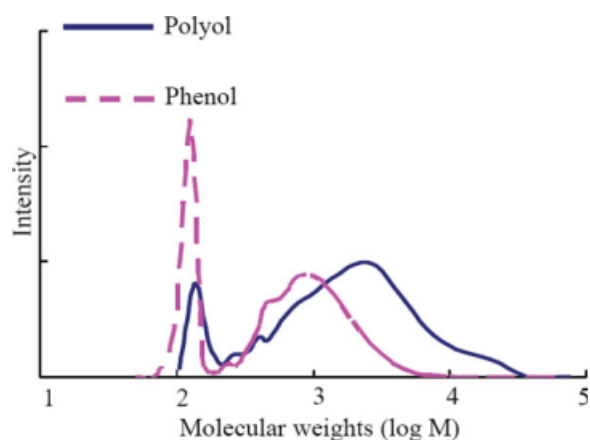


Figure 1 Molecular weight distribution curves of liquefied ma bamboo. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

whereas the high-molecular-weight region included decomposed wood components and their derivatives.³¹

Properties of copolymer epoxy resins

In this study, an excess of epichlorohydrin was employed to react with bisphenol A and liquefied ma bamboo for preparing the copolymer epoxy resins. The amount of reagents used and the properties of resins prepared are shown in Table II. The control, a neat epoxy resin, had viscosity of 3480 cps, nonvolatile content of 90.0%, and EEW of 241.3. However, properties of copolymer epoxy resins, prepared by substituting part of bisphenol A with liquefied bamboo, differed from those of the neat epoxy resin, especially for copolymer epoxy resins prepared with polyhydric alcohol-liquefied bamboo.

When phenol-liquefied bamboo was employed to prepare copolymer epoxy resins, it will also be glycidylated by the epichlorohydrin, so the EEW will not change much as comparing with the neat epoxy resin. Nevertheless, the copolymer epoxy resin that used 10% of liquefied bamboo to replace bisphenol A had viscosity of 8840 cps. However, the viscosity of copolymer epoxy resin decreased as the ratio of liquefied bamboo increased. It may due to the presence of more amount of monofunctional phenyl glycidyl ether.

On the other hand, when part of bisphenol A were replaced by polyhydric alcohol-liquefied bamboo, both the viscosity and EEW of copolymer epoxy resins raised with the ratio of liquefied bamboo increased. Because the polyhydric alcohol-liquefied bamboo had a lower hydroxyl value than phenol-liquefied bamboo, it means that a much more weight of liquefied bamboo should be added to the reaction system to obtain the same amount of hydroxyl group. However, the polyhydric alcohol-liquefied bamboo had a greater molecular weight than that of phenol-liquefied wood. It might lead copolymer epoxy resins with a higher viscosity and EEW.

Figure 2 shows the molecular weight distribution of neat epoxy resin and copolymer epoxy resins. As can be seen, the molecular weight of neat epoxy resin was separated into four regions, namely 308, 432, 701, and 1285. According to Scheme 1, the chemical structure of diglycidyl ether of bisphenol A epoxy resin, polymerization with the value of n as 0, 1, 2, and 3 had the theoretical molecular weight of 340, 620, 900, and 1180, respectively. Therefore, these four regions were attributed to epoxy resin with different degrees of polymerization. However, some peaks had higher molecular weight than the theoretical molecular weight. It might due to some of the

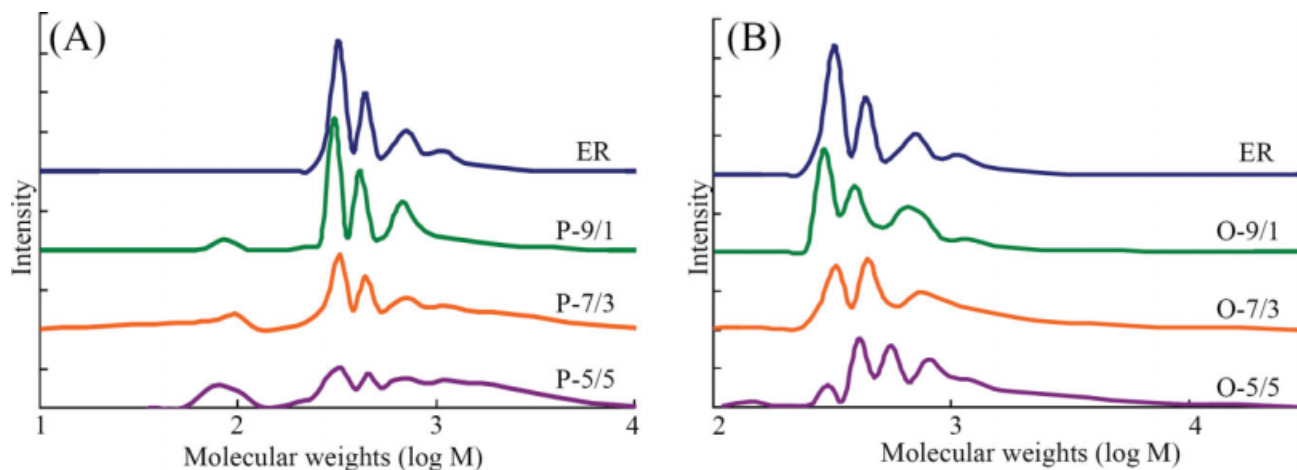
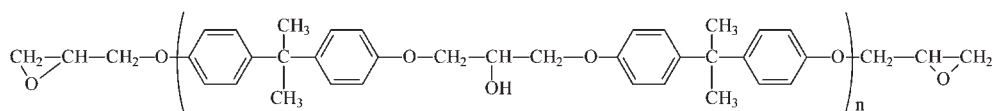


Figure 2 Molecular weight distribution curves of copolymer epoxy resins: (A) Resins prepared with phenol-liquefied bamboo and (B) resins prepared with polyhydric alcohol-liquefied bamboo. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 1 Structure of diglycidyl ether of bisphenol A epoxy resin.

hydroxyl groups in the diglycidyl ether of bisphenol A epoxy resin would react with the epichlorohydrin and formed an appendant glycidyl ether, and increased the molecular weight.³²

The molecular weight distribution of copolymer epoxy resins was similar separated into four regions. However, their distribution tended to a higher molecular weight, and the distinction of these four regions became less clear as the ratio of liquefied bamboo added increased. It indicated that some of the liquefied bamboo participated in the copolymerization. In addition, Figure 2(A) showed that copolymer epoxy resins prepared with phenol-liquefied bamboo appeared some components with the molecular weight around 100, it may be attributed to the free phenol and its glycidyl ether.

Table III shows the average molecular weight of neat epoxy resin and copolymer epoxy resins. Copolymer epoxy resins had higher weight-average molecular weight and molecular weight dispersion than the neat epoxy resin. Increasing the amount of liquefied bamboo substituted would increase the weight-average molecular weight and molecular weight dispersion. It was due to the higher molecular weight for liquefied bamboo than bisphenol A.

Curing behavior of copolymer epoxy resins

Figure 3 shows the variation in temperature of different epoxy resins during the curing reaction under room temperature when the crosslinking reagent,

TETA, was added. The gel time and the weight retention of cured resins after soaking in acetone are shown in Table IV. The results showed that the neat epoxy resin could cure at room temperature, and their curing process was an exothermic reaction. When the temperature reached 50–60°C, the exothermic phenomenon became drastic and was accompanied with a rapid increase in viscosity. The curing phenomenon occurred at the maximum temperature of about 140°C at the time of 10 min.

The curing behavior of copolymer epoxy resins prepared with phenol-liquefied bamboo was similar to that of neat epoxy resin as shown in Figure 3. However, the rate of temperature increasing and the phenomenon of resin curing were faster than those of the neat epoxy resin. It might be due to the synergistic effect of phenol and amine existing simultaneously in copolymer epoxy resins on the curing reaction³³ and the presence of more numbers of electron withdrawing aromatic rings.

When polyhydric alcohol-liquefied bamboo was employed to prepare copolymer epoxy resins, the resin with 10% of bisphenol A being substituted by liquefied bamboo had an obvious heat release and would cure at the time of 9.5 min. However, when the amount of substituted bisphenol A increased to 30 and 50%, the exothermic phenomenon diminished greatly. This result indicates that only a limited amount of polyhydric alcohol-liquefied bamboo could participate in the copolymerization of copolymer epoxy resins due to lack for electron withdrawing aromatic ring.

TABLE III
Average Molecular Weights and Polydispersity of Copolymer Epoxy Resins

Resin code	Synthesis conditions						Average molecular weight ^a		
	First stage		Second stage				M_w	M_n	M_w/M_n
	Epichlorohydrin (mol)	Bisphenol A (mol)	Epichlorohydrin (mol)	Liquefied bamboo					
				Reagent	Hydroxyl group (mol)				
ER	5	1	–	–	–	524	421	1.2	
P-9/1 ^b	4.5	0.9	0.5	Phenol	0.1	592	381	1.5	
P-7/3	3.5	0.7	1.5	Phenol	0.3	848	385	2.2	
P-5/5	2.5	0.5	2.5	Phenol	0.5	963	353	2.7	
O-9/1	4.5	0.9	0.5	Polyol	0.1	589	424	1.4	
O-7/3	3.5	0.7	1.5	Polyol	0.3	888	497	1.8	
O-5/5	2.5	0.5	2.5	Polyol	0.5	1091	566	1.9	

^a M_w , weight-average molecular weight; M_n , number-average molecular weight; M_w/M_n , polydispersity.

^b Bisphenol A/liquefied bamboo.

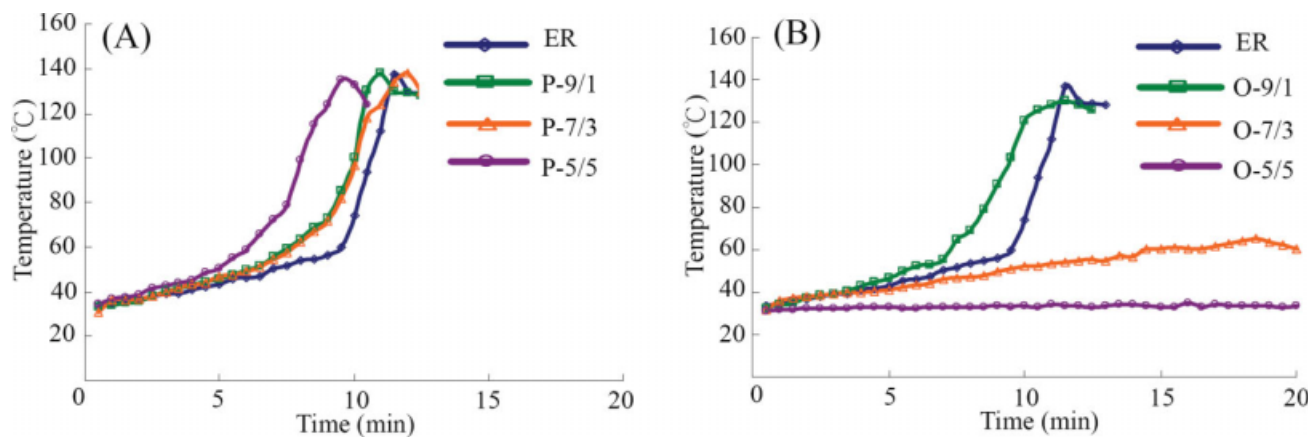


Figure 3 Temperature variations of copolymer epoxy resins during curing: (A) Resins prepared with phenol-liquefied bamboo and (B) resins prepared with polyhydric alcohol-liquefied bamboo. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The weight retention of cured resins after solvent immersed was usually employed to express the degree of curing. As shown in Table IV, the cured neat epoxy resin had weight retention of 90.3% after being immersed in acetone. The copolymer epoxy resin with 50% of bisphenol A substituted by phenol-liquefied bamboo had weight retention of 87.2%. It indicates that phenol-liquefied bamboo could be employed to prepare the epoxy resins with the similar curing degree as those of the neat epoxy resin even with half of bisphenol A being replaced. However, it was not suitable for polyhydric alcohol-liquefied bamboo.

DSC thermoanalysis of copolymer epoxy resins

The DSC thermoanalysis was carried out with a three-stage scanning method. Figure 4 shows the heat flow of isothermal analysis of epoxy resin and copolymer epoxy resins, with 30% of bisphenol A

substituted by liquefied bamboo, after mixing with TETA. As can be seen, copolymer resins showed an exothermic peak at the initial stage of curing reaction, but the exothermic phenomenon for the neat epoxy resin appeared later than that of copolymer epoxy resins.

Figure 5 shows the DSC thermoscaning thermograms after the isothermal analysis. They showed an endothermic peak at lower temperature followed by an obvious exothermic peak at higher temperature. The endothermic peak might be due to the evaporation of curing reagent that had not reacted after the first stage of isothermal curing reaction. The exothermic peak at higher temperature was attributed to the postcuring reaction, indicating that the resin had not completely cured at the isothermal curing stage, which took place at 30°C for 4 h.

After the second stage, a similar thermoscaning process was repeated, and the thermogram was shown in Figure 6. As can be seen, both the neat

TABLE IV
Curing Properties and Gel Degree of Copolymer Epoxy Resins

Resin code	Synthesis conditions							Weight retention (%)
	First stage		Second stage					
	Epichlorohydrin (mol)	Bisphenol A (mol)	Epichlorohydrin (mol)	Liquefied bamboo		Curing time (min)		
				Reagent	Hydroxyl group (mol)			
ER	5	1	—	—	—	10.0	90.3	
P-9/1 ^a	4.5	0.9	0.5	Phenol	0.1	10.0	87.3	
P-7/3	3.5	0.7	1.5	Phenol	0.3	9.5	87.5	
P-5/5	2.5	0.5	2.5	Phenol	0.5	8.0	87.2	
O-9/1	4.5	0.9	0.5	Polyol	0.1	9.5	85.1	
O-7/3	3.5	0.7	1.5	Polyol	0.3	87.0	73.1	
O-5/5	2.5	0.5	2.5	Polyol	0.5	— ^b	— ^b	

^a Bisphenol A/liquefied bamboo.

^b Uncured.

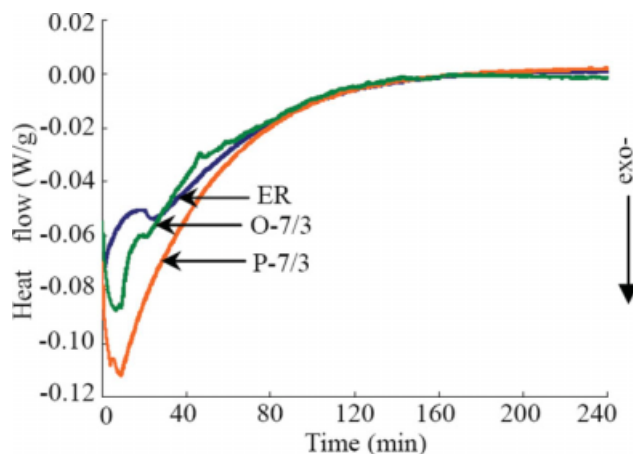


Figure 4 Isothermal DSC thermograms of epoxy resin and copolymer epoxy resins cured by TETA (copolymer epoxy resins prepared with 30% of bisphenol A substituted by liquefied bamboo). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

epoxy resin and the copolymer epoxy resin prepared with polyhydric alcohol-liquefied bamboo displayed a glass transition phenomenon. Nevertheless, the same was not observed for the copolymer epoxy resin prepared with phenol-liquefied bamboo. These results indicated that introducing phenol-liquefied bamboo into the epoxy resin could provide a higher crosslinking density, and bring the cured resin to a more complete net structure. The glass transition temperature of the neat epoxy resin and copolymer resin prepared with polyhydric alcohol-liquefied bamboo was 89.6°C and 73.0°C, respectively. The lower glass transition temperature of the copolymer resin prepared with polyhydric alcohol-liquefied

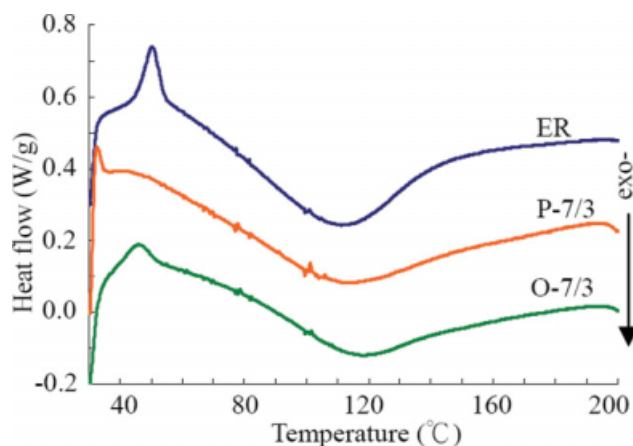


Figure 5 DSC thermal scanning thermograms of isotherm-cured copolymer epoxy resins (copolymer epoxy resins prepared with 30% of bisphenol A substituted by liquefied bamboo). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

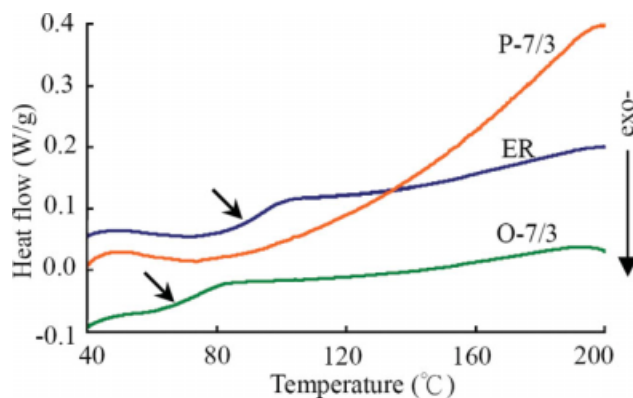


Figure 6 DSC thermograms of full-cured epoxy resin and copolymer epoxy resins (copolymer epoxy resins prepared with 30% of bisphenol A substituted by liquefied bamboo). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bamboo was due to the longer polyether chain in the PEG, which would cause the cured resin to have a lower crosslinking density.

TGA thermoanalysis of copolymer epoxy resins

Figure 7 shows the TG and DTG curves of cured resins. As shown in TG curves, the thermal degradation of cured resins mainly occurred at the temperature between 200 and 400°C. The neat epoxy resin and copolymer epoxy resin that prepared with polyhydric alcohol-liquefied bamboo showed a similar thermal degradation trend. Nevertheless, the DTG curves showed a significant difference between the neat epoxy resin and copolymer epoxy resins. For the neat epoxy resin, the DTG curve appeared only one peak that had the fastest thermal degradation rate at 330°C and a shoulder at 260°C. Nevertheless, the fastest thermal degradation rate temperature of both the copolymer epoxy resins shifted to 285°C. It was due to the lignocellulose components that introduced from the liquefied bamboo were rapidly thermodegraded at this temperature. However, copolymer epoxy resin prepared with phenol-liquefied bamboo had a slower thermal weight loss and higher char content at the temperature up to 700°C. It is because the aromatic structure of phenol-liquefied bamboo present in the cured resin serves as the free radical trapper, thus delaying the thermal degradation. Moreover, the large amount of aromatic structure would form a char layer that could serve as a heat conduction shield, and increase the thermal stability of the cured resin.^{34,35}

CONCLUSIONS

Bisphenol A and either phenol- or polyhydric alcohol-liquefied ma bamboo were reacted with

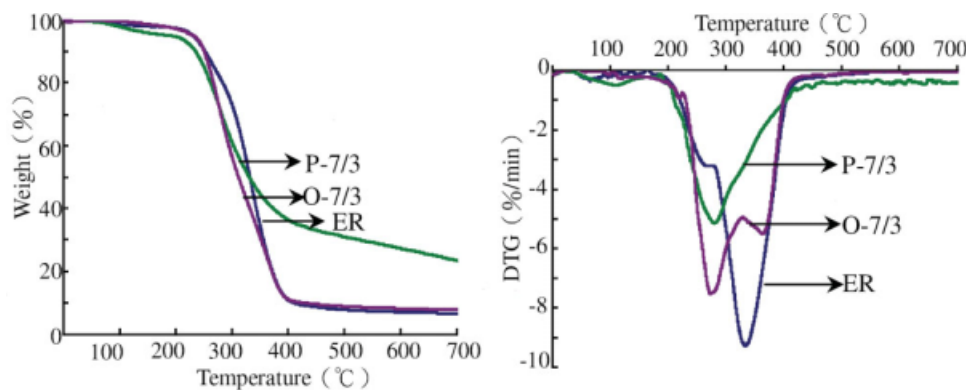


Figure 7 TG and DTG curves of cured epoxy resin and copolymer epoxy resins (copolymer epoxy resins prepared with 30% of bisphenol A substituted by liquefied bamboo). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

epichlorohydrin to prepare liquefied bamboo-bisphenol A copolymer epoxy resins. The results showed that liquefied ma bamboo could be used as raw materials to prepare copolymer epoxy resins, which had the capability of curing at room temperature by the addition of TETA. However, using phenol-liquefied ma bamboo as raw material was more suitable than that using polyhydric alcohol-liquefied ma bamboo as raw material. Even when half of the bisphenol A was replaced with phenol-liquefied ma bamboo, the resulting copolymer resins still had good reactivity, and the cured resin had high-weight retention after being immersed in acetone. Moreover, postheating treatment could promote room temperature-cured resins to undergo an advanced crosslinking reaction. The copolymer epoxy resins prepared with phenol-liquefied bamboo also had a better thermal stability, lower thermal weight loss rate, and higher residual char content.

References

- Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Holzfor-schung* 1996, 50, 85.
- Alma, M. H.; Basturk, M. A. *Ind Crop Prod* 2006, 24, 171.
- Lee, S. H.; Yoshioka, M.; Shiraishi, N. *J Appl Polym Sci* 2000, 77, 2901.
- Lee, S. H.; Teramoto, Y.; Shiraishi, N. *J Appl Polym Sci* 2002, 84, 468.
- Chen, Y. C.; Lee, W. J.; Liu, C. T. *Forest Prod Ind* 2006, 25, 249.
- Chen, Y. C.; Lee, W. J.; Liu, C. T. *Q J Forest Res* 2007, 29, 55.
- Chen, Y. C.; Lee, W. J. *Taiwan J Forest Sci* 2008, 23, 221.
- Lee, W. J.; Liu, C. T. *J Appl Polym Sci* 2003, 87, 1837.
- Lee, W. J.; Chang, K. C.; Sung, I. C.; Chen, Y. C. *Q J Chin For-est* 2006, 39, 517.
- Lee, W. J.; Chen, Y. C. *Bioresour Technol* 2008, 99, 7247.
- Wu, C. C.; Lee, W. J. *Prod Ind* 2007, 26, 95.
- Kurimoto, Y.; Takeda, M.; Doi, S.; Tamura, Y.; Ono, H. *Bioresour Technol* 2001, 77, 33.
- Kurimoto, Y.; Takeda, M.; Koizumi, A.; Yamauchi, S.; Doi, S.; Tamura, Y. *Bioresour Technol* 2000, 74, 151.
- Lee, S. H.; Yoshioka, M.; Shiraishi, N. *J Appl Polym Sci* 2000, 78, 319.
- Wei, Y.; Cheng, F.; Li, H.; Yu, J. *J Appl Polym Sci* 2005, 95, 1175.
- Lee, W. J.; Chang, C. F. *Q J Chin Forest* 2007, 40, 405.
- Wu, H. H.; Wu, C. C.; Lee, W. J. *Q J Forest Res* 2008, 30, 65.
- Lee, W. J.; Lin, M. S. *J Appl Polym Sci* 2008, 109, 23.
- Kobayashi, M.; Tukamoto, K.; Tomita, B. *Holzfor-schung* 2000, 54, 93.
- Kobayashi, M.; Hatano, Y.; Tomita, B. *Holzfor-schung* 2001, 55, 667.
- Asano, T.; Kobayashi, M.; Tomita, B.; Kajiyama, M. *Holzfor-schung* 2007, 61, 14.
- Kishi, H.; Fujita, A.; Miyazaki, H.; Matsuda, S.; Murakami, A. *J Appl Polym Sci* 2006, 102, 2285.
- Wu, C. C.; Lee, W. J. *Forest Prod Ind* 2008, 27, 31.
- Yamada, T.; Ono, H. *Bioresour Technol* 1999, 70, 61.
- Lin, L.; Yao, Y.; Shiraishi, N. *Holzfor-schung* 2001, 55, 617.
- Lin, L.; Yao, Y.; Yoshioka, M.; Shiraishi, N. *Carbohydr Polym* 2004, 57, 123.
- Kobayashi, M.; Asano, T.; Kajiyama, M.; Tomita, B. *J Wood Sci* 2004, 50, 407.
- Lee, W. J.; Chang, C. *Forest Prod Ind* 2003, 22, 205.
- Yao, Y.; Yoshioka, M.; Shiraishi, N. *J Appl Polym Sci* 1996, 60, 1939.
- Zhang, Y.; Ikeda, A.; Hori, N.; Takemura, A.; Ono, H.; Yamada, T. *Bioresour Technol* 2006, 97, 313.
- Kurimoto, Y.; Koizumi, A.; Doi, S.; Tamura, Y.; Ono, H. *Bio-mass Bioenerg* 2001, 21, 381.
- Garea, S.-A.; Corbu, A.-C.; Deleanu, C.; Iovu, H. *Polym Test* 2006, 25, 107.
- Gao, Y.; Yu, Y. *J Appl Polym Sci* 2003, 89, 1869.
- Duanna, Y. F.; Liu, T. M.; Cheng, K. C.; Su, W. F. *Polym Degrad Stab* 2004, 84, 305.
- Tyberg, C. S.; Bergeron, K.; Sankarapandian, M.; Shih, P.; Loos, A. C.; Dillard, D. A.; Mcgrath, J. E.; Riffle, J. S.; Sorathia, U. *Polymer* 2000, 41, 5053.