

ORIGINAL ARTICLE

Curing and thermal properties of copolymer epoxy resins prepared by copolymerized bisphenol-A and epichlorohydrin with liquefied *Dendrocalamus latiflorus*

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Dendrocalamus latiflorus Munro (ma bamboo) was liquefied in phenol or in polyethylene glycol/glycerol cosolvent, with H₂SO₄ as a catalyst. The liquefied bamboo was reacted with bisphenol-A and epichlorohydrin to prepare copolymer epoxy resins. The thermal properties of resins during and after curing were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The results showed that a novel epoxy resin can be prepared by copolymerizing liquefied bamboo with bisphenol-A and epichlorohydrin in a two-step process. DSC analysis showed that the copolymer epoxy resins prepared with phenol-liquefied bamboo had a curing behavior similar to that of neat epoxy resin, even when 50% of the bisphenol-A was replaced with liquefied bamboo. However, the reactivity of copolymer epoxy resins prepared with polyhydric alcohol-liquefied bamboo decreased as the substitution amount of liquefied bamboo increased. DMA showed that the storage modulus and $\tan \delta$ of cured copolymer epoxy resins decreased as the amount of substituted liquefied bamboo increased.

Polymer Journal (2010) 42, 711–715; doi:10.1038/pj.2010.64; published online 4 August 2010

Keywords: curing behavior; epoxy resin; liquefied *Dendrocalamus latiflorus*; thermal property

INTRODUCTION

Solvent liquefaction is one method for converting biomass from a solid to a liquid. The liquefied biomasses are multihydroxy compounds and can be used to prepare various types of synthetic resins depending on the kind of solvent used. Currently, phenol and polyhydric alcohol are the most widely used solvents. Phenol-liquefied biomasses can be used to prepare resol and novolac phenol-formaldehyde resins.^{1–4} In another liquefaction system, polyliquefied biomasses can be used to prepare polyurethane resins.^{5–8}

Epoxy resin is one of the most important resins and has been widely used for various industry products, such as adhesives, coatings and moldings. Many types of epoxy resins with different properties have been prepared. The bisphenol-A type is the most commonly used epoxy resin: it is a prepolymer prepared by reacting bisphenol-A with epichlorohydrin. However, use of bisphenol-A is often undesirable because it can mimic the body's own hormones and may lead to negative health effects.^{9,10}

Therefore, determining how to reduce the amount of bisphenol-A while maintaining the performance of the resin is a significant problem that attracts much interest. One possible solution to this problem that has been investigated by some researchers involves blending liquefied wood with epoxy resin. The resulting resin can be used as an adhesive for wood bonding.^{11–15} This new resin not only

decreases the amount of bisphenol-A in the cured resins but also promotes the use of renewable biomass.

Bamboo is one of the most important forest products in Taiwan. It is an enormous potential renewable resource because of its fast growth. After the bamboo shoots emerge from the ground, their diameter increases rapidly, and they grow to their full height in ~60–70 days. In our previous study,¹⁶ phenol- and polyhydric alcohol-liquefied bamboos were used to react with bisphenol-A and epichlorohydrin to prepare copolymer epoxy resin in a two-step copolymerization process. In this study, the curing behavior and thermal properties of these copolymer epoxy resins during the curing reaction and after being cured were measured with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

EXPERIMENTAL PROCEDURE

Materials

Dendrocalamus latiflorus Munro (ma bamboo), ~5 years of age, was felled and collected from Nantou in central Taiwan. It was air dried and ground to powder in a hammer mill with a 2-mm-diameter screen. The powders passing the 20-mesh sieve were dried in an oven at 105 °C for 24 h before liquefaction. Polyethylene glycol (PEG 400; Katayama Chemical Co., Osaka, Japan), glycerol, phenol and sulfuric acid (Union Chemical Co., Taipei, Taiwan) were used for liquefaction. Bisphenol-A (Hayashi Chemical Co., Kyoto, Japan), epichlorohydrin

(Tedia Chemical Co., Fairfield, OH, USA) and sodium hydroxide (Shimadzu Co., Osaka, Japan) were used for the epoxy resin synthesis. Triethylene tetramine (TETA; Hayashi Chemical Co.) was used as the curing hardener for the epoxy resins. All chemicals were of reagent grade and were used without further purification.

Liquefaction of ma bamboo

For liquefying ma bamboo, phenol or polyethylene glycol/glycerol cosolvent (9/1; w/w) was used as the solvent. The optimized liquefaction condition for each solvent was decided according to our previous studies.¹⁶ At the first stage, 450 g solvent was premixed with 13.5 g sulfuric acid (3% based on the weight of the solvent) in a 1000-ml separable glass flask equipped with a stirrer, thermometer and reflux condenser, and heated to 130 and 150 °C for phenol and polyhydric alcohol, respectively. Thereafter, 150 g of ma bamboo powder was gradually added into the reactor. The weight ratio of liquefaction solvent to ma bamboo was 3/1 (w/w). After adding the entire bamboo powder, liquefaction was conducted under constant heating and stirring for 60 and 75 min for the phenol and polyhydric alcohol solvents, respectively. The phenol- and polyhydric alcohol-liquefied bamboo had residue contents of 2.2 and 5.7%, nonvolatile matter of 68.9 and 32.8%, hydroxyl values of 333.7 and 245.3, and average molecular weights of 759 and 2119, respectively.¹⁶

Synthesis and properties of liquefied bamboo/bisphenol-A copolymer epoxy resins

Copolymer epoxy resins were synthesized by a two-step process, as shown in Table 1. The total amount of epichlorohydrin used was 5 mol. In the first step, a mixture of epichlorohydrin and bisphenol-A with a molar ratio of 5:1 was charged into a four-neck glass reaction flask, and the reaction occurred at 110 °C for 2 h under continuous stirring and dripping of NaOH_(aq). Additional epichlorohydrin (0.5, 1.5, 2.5 mol) and a calculated amount of liquefied bamboo (0.1, 0.3, 0.5 mol hydroxyl group) were then added. Copolymerization proceeded under continuous dripping of the remaining NaOH_(aq) over 2 h at the same temperature. The total amount of NaOH added was 1 mol. Finally, the reaction was continued with stirring for another 1 h and cooled to room temperature. The by-product of NaCl was removed by filtration, and the water and unreacted epichlorohydrin were removed by reduced pressure distillation. The viscosity and the epoxy equivalent weight (EEW) of the prepared resins were measured.¹⁶

DSC thermoanalysis of copolymer epoxy resins

DSC thermoanalysis was carried out by a differential scanning calorimeter (Perkin-Elmer DSC-7, Perkin-Elmer, Waltham, MA, USA). The epoxy resin was mixed completely with TETA of an equivalent weight based on the epoxy group and amino group and quickly sealed in the aluminum capsule used for DSC analysis. The sample was heated from 30 to 200 °C at a heating rate of 10 °C min⁻¹. The variation in heat flow during the period of heat scanning was detected and the relative thermal parameters were calculated.

DMA of copolymer epoxy resins

The curing behavior of liquefied bamboo-based epoxy resins and the thermal mechanical properties of cured resins were investigated with a dynamic mechanical analyzer (Perkin-Elmer DMA 8000). To analyze curing behavior, the resin was mixed with an equivalent weight of TETA, as described in the DSC analysis, and was evenly spread on the surface of an aluminum pocket. The test was carried out by the method of three-point bending at temperatures from 25 to 150 °C, with a heating rate of 10 °C min⁻¹ and an oscillation frequency of 1.0 Hz. To determine the thermal mechanical properties of the cured resin, resins mixed with TETA were poured into a mold and cured at room temperature for 2 days. The thermal mechanical properties of cured resins were determined using compression tests at temperatures from 25 to 180 °C, with a heating rate of 2 °C min⁻¹ and an oscillation frequency of 1.0 Hz.

RESULTS AND DISCUSSION

Properties of copolymer epoxy resins

Copolymer epoxy resins were prepared using a two-step process in which 10, 30 and 50% of bisphenol-A was replaced with liquefied bamboo. Neat epoxy resin prepared with a molar ratio of epichlorohydrin to bisphenol-A of 5:1 was used as the control. The synthesis conditions and properties of resins prepared are shown in Table 1. The neat epoxy resin had a viscosity of 3480 c.p.s. and an EEW of 241.3. When phenol-liquefied bamboo was used to prepare epoxy resins, the resins prepared had EEW values that were similar to those of neat epoxy resins. In contrast, when some of the bisphenol-A was replaced with polyhydric alcohol-liquefied bamboo, both the viscosity and EEW of the prepared resins increased with increased dosage of liquefied bamboo. A more detailed discussion is provided in our previous article.¹⁶

Curing behavior of copolymer epoxy resins

In our previous study,¹⁶ the curing properties of liquefied bamboo-based epoxy resins under room temperature were measured. Results showed that copolymer epoxy resins could cure at room temperature after the hardener was added. However, heat treatment could enhance the crosslinking of copolymer epoxy resins that cured at room temperature. In this study, both DSC and DMA with heat scanning were used to investigate the curing behavior of copolymer epoxy resins to obtain advanced information about these resins. Figure 1 shows the variation in heat flow of various resins during the period of DSC heat scanning. All resins showed an exothermic peak; however, the heat flow variation of copolymer epoxy resins prepared with phenol-liquefied bamboo was quite different from those prepared with

Table 1 Synthesis conditions and properties of copolymer epoxy resins

Resin code	Synthesis conditions						
	First stage			Second stage			
	Epichlorohydrin (mol)	Bisphenol A (mol)	Epichlorohydrin (mol)	Liquefaction reagent	Hydroxyl group (mol)	Viscosity (c.p.s.)	EEW
ER	5	1	—	—	—	3480	241.3
P-9/1	4.5	0.9	0.5	Phenol	0.1	8840	266.5
P-7/3	3.5	0.7	1.5	Phenol	0.3	7080	264.3
P-5/5	2.5	0.5	2.5	Phenol	0.5	2953	254.8
O-9/1	4.5	0.9	0.5	Polyol	0.1	6780	265.0
O-7/3	3.5	0.7	1.5	Polyol	0.3	19780	366.9
O-5/5	2.5	0.5	2.5	Polyol	0.5	29840	1173.4

Abbreviation: EEW, epoxy equivalent weight.

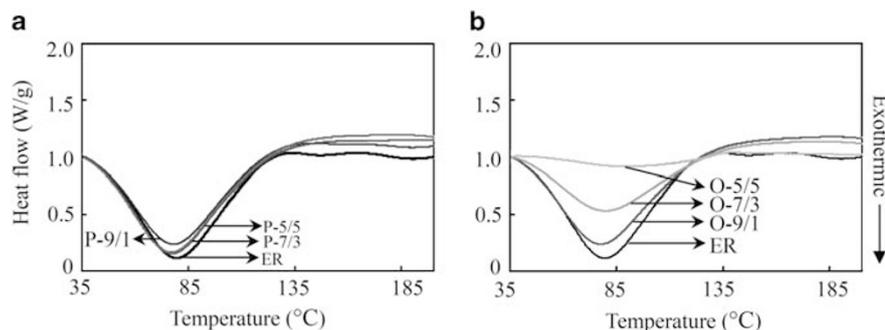


Figure 1 DSC curves of copolymer epoxy resins with 10 phr of TETA during the period of thermosetting. (a) and (b) were prepared with phenol- and polyhydric alcohol-liquefied bamboo, respectively.

polyhydric alcohol-liquefied bamboo. In Figure 1a, all of the copolymer epoxy resins with phenol-liquefied bamboo had heat flow curves similar to that of neat epoxy resin, indicating that they had the same curing behavior. But Figure 1b shows that when polyhydric alcohol-liquefied bamboo was used as the raw material, the height of the exothermic peak decreased as the substitution amount of liquefied bamboo increased, indicating that less crosslinking reactions occurred during the curing period. The different exothermic tendency between phenol-liquefied bamboo-based and polyhydric alcohol-liquefied bamboo-based copolymers could be due to the former having monofunctional phenyl glycidyl ethers and thus having more electron-withdrawing aromatic rings than the latter.¹⁶

Table 2 shows the thermoanalysis parameters of liquefied bamboo-based epoxy resins as calculated from the exothermic peak. The neat epoxy resin had an onset temperature of 46.8 °C, peak temperature of 79.8 °C, reaction heat of 243.8 J g⁻¹ and peak height of 0.92 W g⁻¹. When some of the bisphenol-A was replaced with phenol-liquefied bamboo, both the onset temperature and the peak temperature decreased, indicating that phenol-liquefied bamboo-based epoxy resins had a higher reactivity than neat epoxy resin. In addition, on increasing the substitution amount of liquefied bamboo, the reaction heat increased. This may occur because the increased amount of aromatics present in liquefied bamboo-based epoxy resins could provide a synergistic effect with amine, the hardener, increasing crosslinking reactions and promoting the curing reaction.¹⁷ The liquefied bamboo-based epoxy resins with 50% bisphenol-A replaced by phenol-liquefied bamboo had a curing heat of 261.5 J g⁻¹, which was higher than that of the others.

However, when a portion of bisphenol-A was replaced with polyhydric alcohol-liquefied bamboo, a negative effect on the curing reaction was observed, especially when 50% of bisphenol-A was replaced. The resulting resin had higher onset and peak temperatures and less heat was released during the curing reaction, indicating a lower reactivity. Earlier in the discussion, it was noted that epoxy resins copolymerized with polyhydric alcohol-liquefied bamboo had a higher EEW, which means they had less content of epoxy groups per unit weight of the resin, and this may result in the reduced crosslinking reaction. Furthermore, the long molecular chain of polyethylene glycol that existed in polyhydric alcohol-liquefied bamboo would also decrease the reactivity of these liquefied bamboo-based epoxy resins and lead to the increased onset and peak temperatures of the curing reaction.

DMA was used to investigate the curing behavior of liquefied bamboo-based epoxy resins. Figure 2 shows the variation in the storage modulus (G') and damping ($\tan \delta$) of various resins during heat curing. The viscoelastic property of thermosetting resins

Table 2 DSC thermoanalysis parameters of copolymer epoxy resins

Resin code	Onset (°C)	Peak (°C)	ΔH (J g ⁻¹)	Peak height (W g ⁻¹)
ER	46.8	79.8	243.8	0.92
P-9/1	43.5	78.9	225.7	0.81
P-7/3	43.2	77.7	253.1	0.90
P-5/5	43.8	77.4	261.5	0.90
O-9/1	41.8	78.9	224.2	0.82
O-7/3	44.0	80.7	161.2	0.51
O-5/5	58.6	92.3	35.8	0.11

Abbreviation: DSC, differential scanning calorimetry.

from viscous liquid to cured solid can be classified into three stages during the period of thermosetting. In the first stage, the resin has lower G' and $\tan \delta$. However, both G' and $\tan \delta$ rapidly increase with temperature up to the beginning of the crosslinking reaction (second stage). After the resins are completely cured, the maintained G' levels off at a maximum value, but the $\tan \delta$ decreases to a lower value (third stage).

The curing of neat epoxy resin (Figure 2a) showed that a rapid curing reaction occurred at 100 °C. However, for the copolymer resin of O-7/3, 30% of bisphenol-A was replaced with polyhydric alcohol-liquefied bamboo, and the curing reaction shifted to a higher temperature, as shown in Figure 2c, indicating that it had lower reactivity. Nevertheless, for those copolymer resins prepared by replacing some of the bisphenol-A with phenol-liquefied bamboo, the variation in G' curves and peak temperatures of $\tan \delta$ were similar to that of neat epoxy resin, even when 50% of bisphenol-A was substituted (Figure 2f).

Thermal mechanical properties of cured copolymer epoxy resins

The thermal dynamic mechanical properties of the cured liquefied bamboo-based epoxy resins were measured with DMA. Figures 3 and 4 show the variation in G' and $\tan \delta$ during the period of heat scanning for phenol- and polyhydric alcohol-liquefied bamboo-based epoxy resins, respectively. The neat epoxy resin had a higher initial G' than the liquefied bamboo-based epoxy resins at the glassy state, indicating that the neat epoxy resin had more stiffness than did the liquefied bamboo-based epoxy resin. But the G' of the liquefied bamboo-based epoxy resin increased when the heating temperature increased, indicating that a post-curing reaction took place. This phenomenon became more obvious and appeared at lower temperatures, as more bisphenol-A was replaced with liquefied bamboo. This result indicates that liquefied bamboo-based epoxy resins did not completely cure at room temperature.

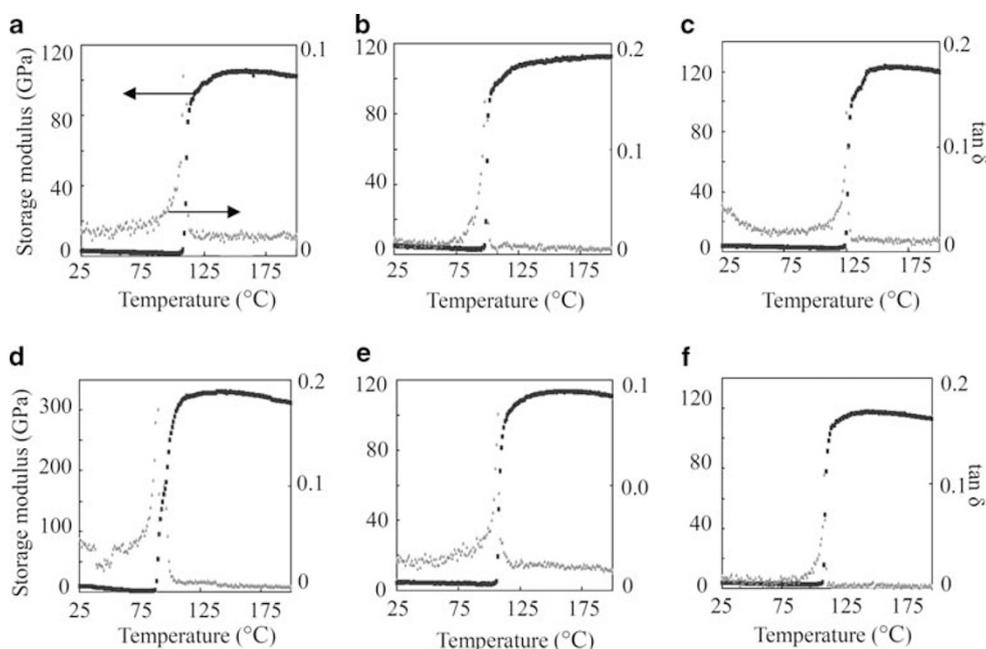


Figure 2 DMA curves of copolymer epoxy resins with 10 phr of TETA during the period of thermosetting. (a) Epoxy resin, (b) O-9/1, (c) O-7/3, (d) P-9/1, (e) P-7/3 and (f) P-5/5.

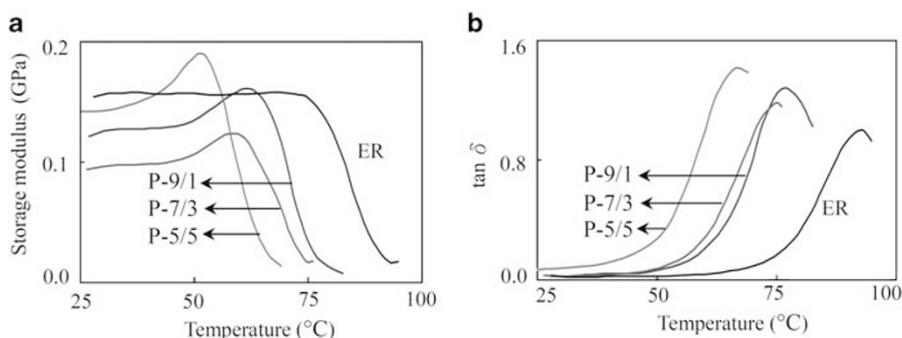


Figure 3 DMA curves of cured copolymer epoxy resins prepared with phenol-liquefied bamboo. (a) and (b) are storage modulus and $\tan \delta$ of cured resin, respectively.

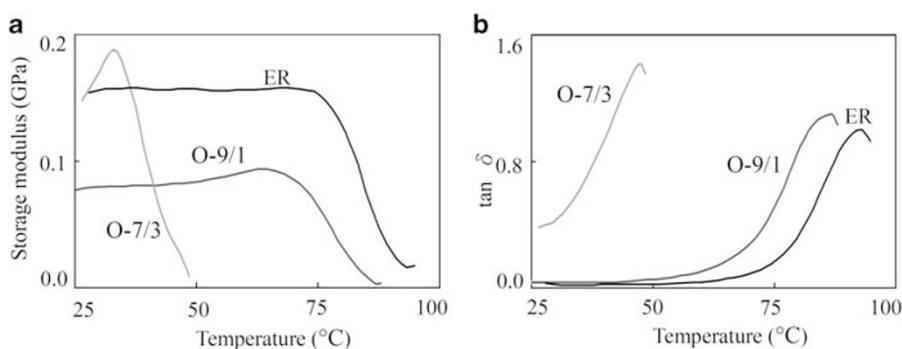


Figure 4 DMA curves of cured copolymer epoxy resins prepared with polyhydric alcohol-liquefied bamboo. (a) and (b) are storage modulus and $\tan \delta$ of cured resin, respectively.

In the previous section, we noted that phenol-liquefied bamboo-based epoxy resins had a curing behavior similar to neat epoxy resin, as described in the DSC thermosetting analysis. However, Figure 3b shows that the peak temperature of $\tan \delta$, which is defined as the glass transition temperature (T_g), was 93.3 °C for the neat epoxy resin but it

shifted to a lower temperature when part of bisphenol-A was replaced with phenol-liquefied bamboo. Moreover, the more bisphenol-A was substituted with liquefied bamboo, the lower the T_g temperature was. For copolymer epoxy resins of P-9/1, P-7/3 and P-5/5, the T_g temperature was 76.3, 74.9 and 66.9 °C, respectively. This result

indicates that cured copolymer epoxy resins have a different network structure from neat epoxy resin and less crosslinking density than neat epoxy resin. These findings may be due to the presence of mono-functional phenyl glycidyl ethers formed by phenol existing in the phenol-liquefied bamboo. Figure 4 shows that copolymer epoxy resins prepared with polyhydric alcohol-liquefied bamboo also had lower G' and $\tan \delta$ than did neat epoxy resin.

CONCLUSION

Phenol- and polyhydric alcohol-liquefied bamboo can be used to replace a portion of bisphenol-A to prepare a novel epoxy resin in a two-stage copolymerization procedure. Copolymer epoxy resins prepared with phenol-liquefied bamboo as a raw material had better curing performance than those prepared with polyhydric alcohol-liquefied bamboo. Phenol-liquefied bamboo had a curing behavior similar to that of neat epoxy resin, even when 50% of bisphenol-A was replaced. However, DMA showed that copolymer epoxy resins cured at room temperature had less crosslinking than neat epoxy resin.

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