Synthesis of Liquefied Corn Barn-Based Epoxy Resins and Their Thermodynamic Properties

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Received 31 March 2011; accepted 8 October 2011
DOI 10.1002/app.36314

ABSTRACT: The liquefied corn barn-based epoxy resin (LCBER) was synthesized through the glycidyl etherification reaction from liquefied corn barn (LCB), which has groups of bound phenol, and epichlorohydrin under alkali conditions. The average molecular weights of LCB and LCBER in various liquefaction conditions were examined. The thermodynamic properties of thermosetting resin cured by polyamide-650 (PA-650) were evaluated. It was found that the macromolecular chain and epoxy function of the resins would be a dominant factor for crosslinking density and properties of the cured LCBER. The cured liquefied CB-based epoxy resin (LCBER-30) using the corresponding LCB at 30 min (LCB-30) as raw materials had much macromolecular exhibited higher glass-transition and decomposition temperatures at 5% weight loss (T_d), but worse shear strength in comparison with the other LCBER ones. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2304–2311, 2012

Key words: liquefaction; corn barn; epoxy resins; synthesis; characterization

INTRODUCTION

In recent years, environmental concern and restricted availability of petrochemical resources have attracted considerable attention, followed by the utilization of renewable biomass, because of its biodegradability, availability, and renewable nature. Liquefaction of biomass is considered to be an effective method for utilizing lignoellulosic materials and can be divided into two categories based on the reaction condition.[1,2] The fist category required high reaction temperature and pressure-proof reactor.[3–5] The second category of liquefaction can be carried out by using reactive solvents, i.e., phenols, polyhydric alcohols, and carbonates, in the presence of strong acid at relatively low temperature, usually at 150°C, under atmospheric pressure.[6–10]

These processes are based on solvolysis of lignocellulosic materials. It is clear that liquefaction products can be applied to raw materials of value-add polymer products with the development of this liquefaction, such as epoxy resin which has the characteristics of good mechanical and adhesive performances.[11–13] However, these works are mainly focused on the effects of polymer blends between the liquefied products and commercial epoxy resin. A wood-based epoxy resin has been made by Kishi et al.,[14] but the interaction relationships between liquefied products and cured wood-based resin are not much discussed. In this study, it is the first time that a novel epoxy resin was synthesized from phenolated corn barn (CB), and the characterization of cured CB-based resin comparing with liquefied CB, such as weight-molecular weight distribution and thermodynamic properties were investigated, especially the relationship between them were outlined in this article.

EXPERIMENTAL

Materials

Corn bran used in liquefaction was obtained from the suburb in Dalian China, which was stripped corn and milled by 20–80 mesh, then dried at 105°C overnight before use. Phenol, sulfuric acid, methanol, magnesium oxide, epichlorohydrin, sodium hydroxide, and acetone were analytical reagent and polyamide-650 was industrial grade.

Liquefaction of CB

CB and phenol were added to a three-necked flask equipped with a reflux condenser and a stirrer. The

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Contract grant sponsor: Dalian urban and rural construction committee; contract grant number: [2010]45

liquid ratio of phenol to CB was from 2 to 6 (w/w) and the reaction temperature was from 120°C to 180°C. The addition level of sulfuric acid as a catalyst was adopted to 98 mg/g CB according to the experiment by Yamada and Ono.[15] After a defined duration, the reactor was rapidly cooled to room temperature with ice water. Then, the product was poured into methanol. The diluted solution was stirred for 10 min and then was filtrated through a glass fiber filter under reduced pressure. The methanol insoluble residue was dried at 105°C for 24 h and weighed for the determination of the percent residue. The sulfuric acid remained in the methanol soluble part was neutralized with magnesium oxide, and the neutralized part solution was once again filtered with a glass fiber filter to remove the salt produced during neutralization process. Liquefied product was obtained by the removal of methanol and free phenol with vacuum distillation.

The residue (undegraded CB) content R expressed by percentage was defined as follows:

$$R(\%) = 100W_i/W_o \tag{1}$$

where W_i is the dry weight of solvent insoluble fraction, and W_o is the dry weight of CB reactant.

The amounts of excess phenol remaining in the phenolated CB were measured by using high performance liquid chromatography (HPLC) and were determined from the obtained HPLC data using the following Eq. (2)[16]:

$$W_u = (SV_s/P) \times C_p. \tag{2}$$

where W_u is the weight of excess phenol in the reaction mixture after the liquefaction, S is the peak area of excess phenol, V_s is the multiplying factor of dilution with methanol, P is the peak area of a standard phenol solution used as a calibration, and C_p is the concentration of the standard phenol solution used as calibration.

And the amount of bound phenol (BP) that reacted with CB components was determined by the following Eq. (3)[17]:

$$\text{BP}(\%) = 100(W_p - W_u)/(W_o - W_i) \tag{3}$$

where W_p is the weight of phenol charged, W_u is the weight of excess phenol, W_o is the dry weight of CB reactant, and W_i is the dry weight of undegraded CB.

Preparation of LCBER

Liquefied corn barn (LCB) and epichlorohydrin were put into a glass flask equipped with a stirring. The molar ratio of epichlorohydrin for BP in LCB was 20. The 30% (w/w) sodium hydroxide aqueous solution was slowly added using a dropping funnel by fourfold molar ratio to the BP in LCB when the reaction temperature reached 100°C. After 240 min maintaining this temperature, the addition reaction of epichlorohydrin was stopped.

The reactant was diluted with acetone, filtered under the reduced pressure. The liquefied corn barn-based epoxy resin (LCBER) obtained after the removal of solvent and excess epichlorohydrin by evaporating using a rotary evaporator under the reduced pressure.

Measurement for epoxy equivalent and epoxy index

The epoxy equivalent of LCBER was determined by the method of hydrochloric acid–acetone according to China National Standard (GB/T 1677-2008), and the epoxy index (epoxide equivalent/kg resin) was calculated based on the epoxy equivalent.

Gel permeation chromatography (GPC)

The molecular weight distributions of LCB and LCBER were determined using gel permeation chromatography system (Viscotek TDA 302, Houston), equipped with a GMH_{HR}-M and a GMH_{HR}-L gel columns in series at 30°C. Tetrahydrofuran (THF) was used as the solvent and mobile phase. The sample was dissolved in THF and the solution was purified by polytetrafluoroethylene membrane before use. The flow rate was 1 mL/min. The weight-average molecular weights were calibrated using monodispersed polystyrene standards.

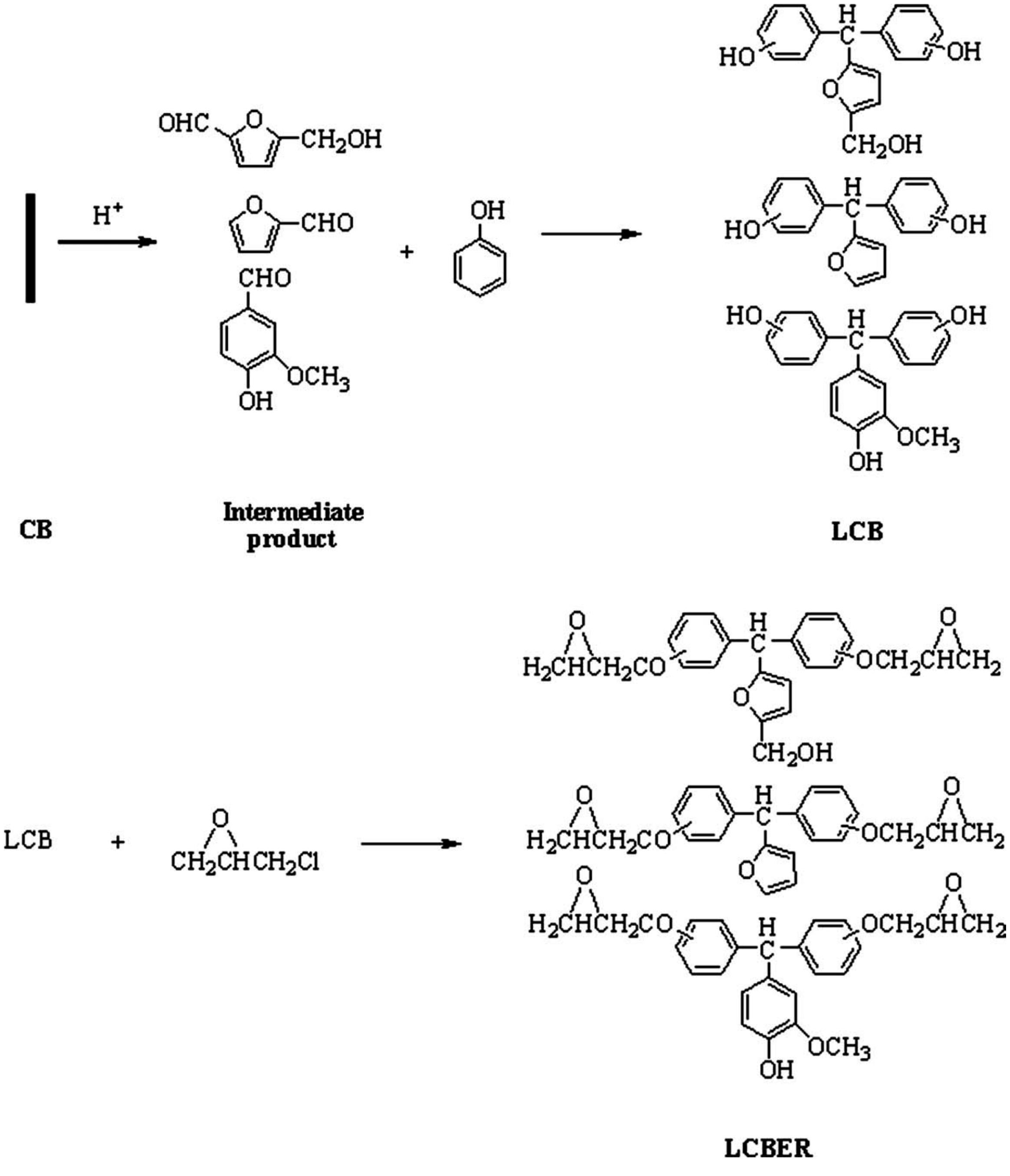
Curing of resin

The LCBER was mixed with polyamide-650 (PA-650) quantatively on a glass plate, and removed quickly onto a pieces of wood (25 mm × 10 mm × 5 mm), to form a 0.2 mm thickness layer, then covered with a same size wood and cured at 80°C for 30 min firstly, then cured continuously at room temperature for 24 h.

Characterization of the cured LCBER

The tensile adhesive shear strength was measured using the RGT-5 universal testing machine (Shenzhen Reger Instrument Co, Shenzhen, China) at the crosshead speed of 1 mm/min according to ISO 6238 : 1987.

The analysis of differential scanning calorimeter (DSC) of the cured LCBER was performed using the NETZSCH-TA4-DSC 204. The temperature-programmed speed was at 10 °C/min from 60 to 300°C under a nitrogen atmosphere.



Scheme 1 The liquefied CB-based epoxy resin mechanism.

Thermogravimetric analysis (TGA) of the cured LCBER was determined using the TGA-Q50-V20.10-Build 36 at the temperature-programmed speed of 10 °C/min from 30 to 500°C under a nitrogen atmosphere.

RESULTS AND DISCUSSION

CB is mainly composed of cellulose, hemi-cellulose, and lignin, which is analogous to wood components. The liquefaction process of phenol liquefaction of CB is also similar to phenol liquefaction of wood, which is a complex process. In one word, the cellulose, hemi-cellulose, and lignin of CB is degraded to intermediate product such as cello-oligosaccharides, glucose, furfural, guaiacol, etc., by sulfuric acid catalyst, then liquefaction product (LCB) is formed by the reaction of phenol and these intermediate product. The LCBER is synthesized through the glycidyl etherification reaction from LCB having groups of BP and epichlorohydrin under alkali conditions.[18–20] The liquefied CB-based epoxy resin mechanism is given in Scheme 1.

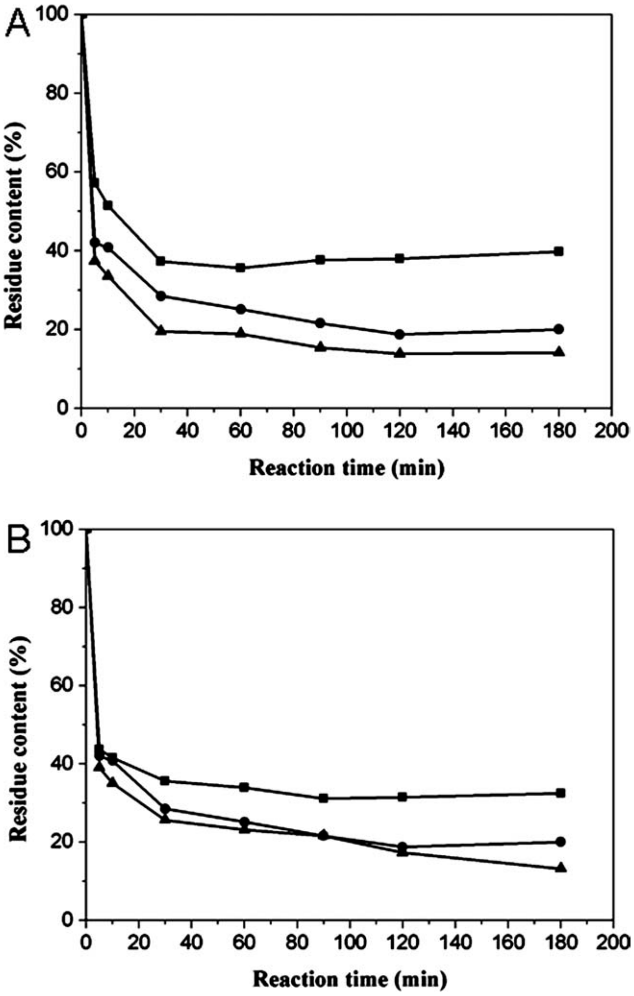


Figure 1 A: Effect of the temperature on the residue yields. The liquid ratio was 4, and the temperatures were (■) 120, (●) 150, and (▲) 180°C. B: Effect of the liquid ratio on the residue yields. The temperature was 150°C and the liquid ratios were (■) 2, (●) 4, and (▲) 6.

Residue content

Figure 1(A) shows the trend of residue content in the liquefaction of CB with the liquefaction time at each temperature. As the reaction temperature rises, the liquefaction proceeds rapidly and the residue content descend to about 14% within 120 min at 180°C, while the residue content is higher at 120 and 150°C compared with 180°C. It obviously indicates that the temperature has a great influence on the liquefaction efficiency. It seems that the degradation of CB can be promoted by rising the reaction temperature. At a low temperature, the lignocellulosic materials degraded slowly; consequently, the residue content decreased at a low speed. When the temperature reached 180°C, the degradation was accelerated, and the residue content was reduced drastically.

The effect of the liquefaction time on the residue content can also be observed in Figure 1(A). In the initial stage of liquefaction, the residue content rapidly decreases, which indicates that the CB are degraded and dissolved rapidly during this stage. The effect of the reaction time on residue content is not so distinct after 30 min of reaction. However, the residue content rises in the last stage of liquefaction, which suggests that the recondensation of the degradation intermediates dominate the reaction at this stage. It has been known that the free-radical fragments formed in the degradation of lignin easily condense to form char in the presence of an acid.[18] The content of the free-radical fragments formed in the degradation of CB increased with the increase in the reaction time. When the concentration of the degradation intermediates is high enough, recondensation occurred easily, and the residue content increased.[8,18] Therefore, the reaction time should not exceed 120 min in the liquefaction with liquid ratio of 4.

Figure 1(B) shows the effect of the liquid ratio on the residue content. The residue content is sensitive to the liquid ratio. The liquefaction efficiency is significantly improved by an increase in the liquid ratio. In the initial stage of liquefaction, the residue content rapidly decreases at each liquid ratio. It generally decreases with increasing liquid ratio. However, the liquefaction behavior for the liquid ratio 6 is quite different from that for the liquid ratio less than 4. Liquefaction behavior seems to be categorized into two types. One is that almost complete liquefaction occurs when reaction is prolonged until 180 min as seen for the liquid ratio of 6. The other is that the residue content rises again in the last stage of liquefaction, resulting in insufficient liquefaction, as seen for the liquid ratio of 2 and 4. The gain of the residue may have two reasons. First, the decomposed fragments would condense via phenols to produce a new sort of high molecular weight in soluble residue if the liquefaction is prolonged.[19] Second, it may be due to the methanol soluble liquefied CB itself transforms into a new residue during the liquefaction.[8] No matter what reason is, it will lead to a rise in the molecular weight of the liquefied CB (Table I). The amount of BP of 180 min is higher than that of 120 min (Fig. 2), and a reasonable explanation can be obtained from the first reason as mentioned above. We conclude that the decomposition, phenolation, and recondensation of the unreacted CB occur with phenol in liquefaction process from 120 min to 180 min, which would lead to the increase of the BP content at 180 min if it is the second reason as mentioned above. Moreover, increasing the liquid ratio is not always effective in improving the liquefaction efficiency. When the liquid ratio exceeds 4, the residue content slightly decreases. Although the residue content at 180 min for the liquid ratio of 6 has an obvious decrease, we

TABLE I
Weight-Average Molecular Weight (M_w), Number-Average Molecular Weight (M_n), and Polydispersity Index (PDI) of Liquefied Products of Various Liquefaction Times and their Corresponding LCBER

Sample	Liquefaction time (min)	M_w	M_n	PDI	Sample	M_w	M_n	PDI
LCB-5	5	467	172	2.8	LCBER-5	590	281	2.1
LCB-10	10	493	219	2.5	LCBER-10	671	276	2.4
LCB-30	30	598	236	2.3	LCBER-30	807	443	1.8
LCB-60	60	563	263	2.1	LCBER-60	779	317	2.5
LCB-90	90	668	323	2.1	LCBER-90	672	340	2.0
LCB-120	120	680	373	1.8	LCBER-120	703	296	2.4
LCB-180	180	710	457	1.6	LCBER-180	720	309	2.3

consider energy saving and environmental protection and select the liquid ratio of 4.

Comparison of the bound phenol of LCB and the epoxy index of LCBER

Figure 2 shows the relationship between the BP of LCB and the reaction time at 150°C for the liquefaction with phenol. The amount of BP becomes increased significantly as the reaction time is extended and it may be due to the dehydration between the phenol and CB components, such as cellulose, hemi-cellulose, and lignin. From Figure 2, it was also observed that the epoxy index of LCBER was synthesized from the LCB. The epoxy index also becomes increased when the reaction time is extended. The synthesis route of LCBER appears to be etherification reaction for the phenolic OH groups in LCB. The epoxy functionality shown as the epoxy index would depend on the amount of BP of LCB.

Molecular weight distribution of LCB and LCBER

Figure 3(A) shows the molecular weight distribution profile of the LCB at 150°C as a function of reaction time. When increasing the reaction time, the molecular weight distributions shift downward. Moreover, as the reaction time increases from 5 to 30 min, both low and high molecular weight parts are drastically diminished, especially, there are some small peaks which represent the low molecular weight fraction reduce gradually until they finally disappear. After this point, the molecular weight distribution becomes stable. Ono reported that lignin was leached out from the wood firstly, then hemi-

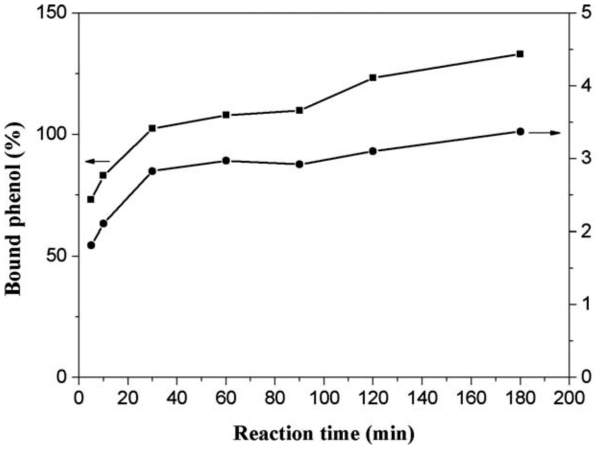


Figure 2 Relationship between the amount of BP of LCB, the epoxy index of LCBER, and the reaction time. The reaction temperature was 150°C, and the liquid ratio was 4.

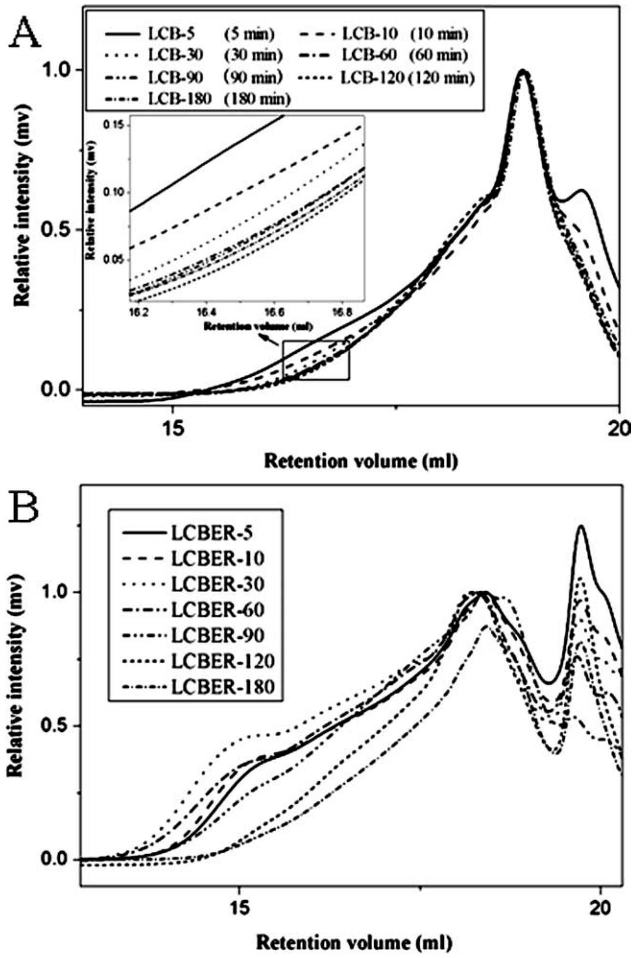


Figure 3 A: GPC diagrams of the LCB obtained in various liquefaction time. B: GPC diagrams of the LCBER synthesized from the corresponding LCB.

cellulose dissolve, and at last cellulose reluctantly dissolve into phenol during the early stage of phenol liquefied wood.[19] Therefore, we can reasonably infer that the low molecular weight fraction is derived from lignin degradations in the CB during liquefaction process and lignin can be degraded completely within 30 min. The corresponding weight-average molecular weight (M_w) and poly-dispersity (M_w/M_n) of the LCB as a function of liquefaction time are summarized in Table I. From the data, M_n is increased and M_w/M_n is decreased with the reaction time extended. Such increase in the M_n of the liquefied products was attributed to the degradation of the lignin, hemi-cellulose, and cellulose in CB during the liquefaction reaction, meanwhile, the increase in M_w leads to a decrease in poly-dispersity, which is very consistent with the results shown in Figure 1. These findings remind us that the liquefaction of CB is divided into two steps based on the liquefaction process and the reaction time. The first step of the liquefaction of CB is to focus on degrading CB and phenolizing lignin of CB before 30 min. The second step is to put more emphasis on phenolizing the decomposed fragments from CB after 30 min.

Figure 3(B) shows the gel permeation chromatography (GPC) diagrams of the LCBER synthesized from the corresponding LCB. The distribution of retention volume of the synthesized resin (LCBER-30) from the corresponding LCB at 30 min is faster than the others and the extreme high molecular weight portion of resin is obtained using the corresponding LCB-30 as raw materials and the M_w value of LCBER-30 is 807. Before or after that, the high molecular weight portion tends to decrease and the M_w values become smaller. In addition, the distribution of the synthesized resin varies with the corresponding LCB and the M_w/M_n of the LCBER (Table I) appears irregular. These discoveries demonstrate that the molecular weight of LCBER is changed during the corresponding LCB. Because the degradation of CB is the dominant reaction in the early stage of liquefaction and the degradation of decomposed fragments is the main reaction in the late stage, the liquefaction 30 min is a significant cut-off point. At this point, the volume of large molecular is more than the other LCB ones, consequently, the corresponding LCBER-30 shows the extreme huge molecular weight portion.

Adhesive properties of LCBER

Mechanical properties of LCBER with polyamide as curing agents are evaluated by universal testing machine. Figure 4 shows the effect of the adhesive shear strength for LCBER thermosets. The results show that the cured resins present good adhesive shear strength and have values ranging from 2.9 to 5.5 MPa. Kishi et al. reported the lap-shear adhesive strength of the wood-based epoxy resin using 4,4′-diamino diphenyl methane (DDM) as curing agent was approximately 5 MPa when the adhesive substrates were plywood.[14] Xie and Chen reported that the epoxy resin was prepared from the liquefied bagasse and diglycidyl ether of bisphenol A and its adhesive shear strength was above 6 MPa.[9] These are evidences that LCBER also have same satisfactory adhesive abilities to plywood than others. This may be probably due to the good affinity (wettability) of LCBER to plywood (biomass material). In other words, the resins include molecules from cellulose, hemi-cellulose and lignin, which have similar chemical structures to the components of the plywood. Moreover, it is noticed that the shear strength of LCBER thermosets first decrease then increase from LCBER-5 to LCBER-180, and was 3.8, 3.1, 2.9 MPa, and 4.1, 4.3, 4.9, 5.5 MPa, respectively. The increase in the amount of epoxy group of LCBER (Fig. 2) should enhance the crosslinking effect, resulting in an increase in the shear strength, but only LCBER-60, LCBER-90, LCBER-120, and LCBER-180 accord with above analysis. This can be due to the fact that lignin is degraded and phenolized completely within 30 min, hemi-cellulose and cellulose are degraded before 30 min, and then are phenolized, which contribute to the extreme huge molecular weight portion of LCBER-30. The result indicates that the shear strength of LCBER thermosets is affected by the molecular weight portion of cellulose and hemi-cellulose. In other words, the amount of epoxy group which is linked in the hemi-cellulose and cellulose chains plays an important role. The less amount of epoxy group they possess in them, the lower cross-linking density and shear strength they have.

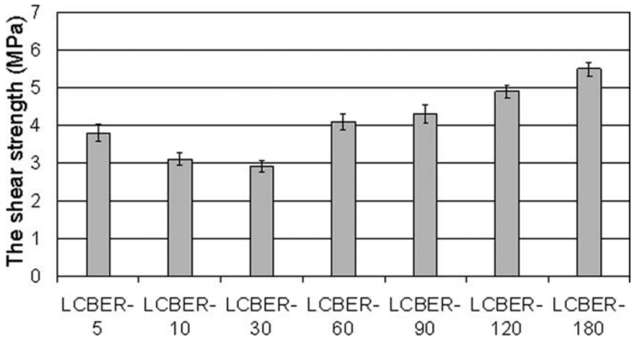


Figure 4 The effect of the adhesive shear strength for cured LCBER.

T_g is an important parameter for thermoset epoxy resins, and in most cases, the service temperature of epoxy-based materials is below their T_g. Therefore, studies on the mechanism of T_g variation and the prediction of T_g decline are critical for the engineering design and application of epoxy resins.[21] T_gs of the cured LCBER are measured by DSC. The DSC

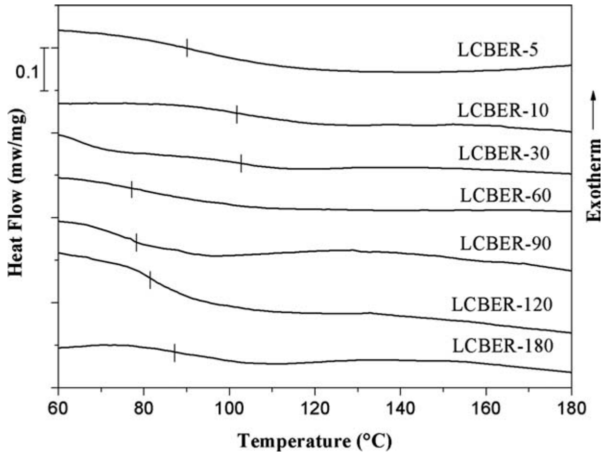


Figure 5 DSC thermograms of the cured LCBER.

thermograms of all the samples using corresponding LCB of different liquefaction time as raw material are displayed in Figure 5, and the results are summarized in Table II. It is noticed that the T_gs of thermoset resin exhibits two main regions according to liquefied products of different liquefaction time. One is LCBER-5, LCBER-10, and LCBER-30 (corresponding to LCB-5, LCB-10, and LCB-30), which has the T_g values ranging from 90.1 to 104.1°C, the other is from LCBER-60 to LCBER-180 (corresponding from LCB-60 to LCB-180), which has the values ranging from 76.1 to 86.4 °C. T_g values of the two regions both have a trend of ascent, which may be attributed to their high cross-linking density because of the increase in epoxy index of LCBER (Fig. 2). However, T_gs of the first region are higher than those of second region, owing to their high rigidity. Yamada and Ono reported that the acid catalyzed liquefaction of cellulose with polyhydric alcohols includes complicated reaction where cellulose was decomposed to glucose, the glucose transforms to 5-hydroxymethylfurfural.[22] Ono et al. reported that cellulose was degraded to cello-oligosaccharides and glucose by sulfuric acid catalyst.[19] The proposed cellulose degradation product may be a major cause of the higher T_gs of the first region. Furthermore, it is noteworthy that T_g of LCBER-30 thermoset resin has a maximum value 104.1°C, owing to the fact that LCBER-30 has the extreme huge molecular weight portion. After liquefaction for 30 min, the molecular weight distribution of LCB and corresponding LCBER becomes narrow, because the large molecular is degraded and phenolized. Hence, the main cause for rising of T_gs in the second region is because of their high cross-linking density, not the high rigidity of large molecular.

TABLE II
Thermal and Mechanical Properties of the Cured LCBER

Sample	T_g (°C)	Temperature at 5 wt % weight loss (°C)	Temperature at rapid weight loss (°C)	Percentage char residue at 600°C (%)
LCBER-5	90.1	243.5	433.0	33.77
LCBER-10	102.0	249.0	434.5	27.23
LCBER-30	104.1	264.5	431.0	27.50
LCBER-60	76.1	227.5	433.0	23.47
LCBER-90	77.4	233.0	437.5	23.02
LCBER-120	81.1	226.0	435.5	26.77
LCBER-180	86.4	213.0	435.5	21.26

Thermal stability of a polymeric material is one of the most important properties for both processing and applications. The TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. TGA thermograms of LCBER containing corresponding LCB of different liquefaction time as substrate are shown in Figure 6, and the obtained data are summarized in Table II. From the data, the LCBER-5, LCBER-10, and LCBER-30 exhibit higher decomposition temperature at 5% weight loss (T_d) compared to the other LCBER ones, and T_d is increased from 243.5°C for LCBER-5 to 264.5°C for LCBER-30, the lowest T_d

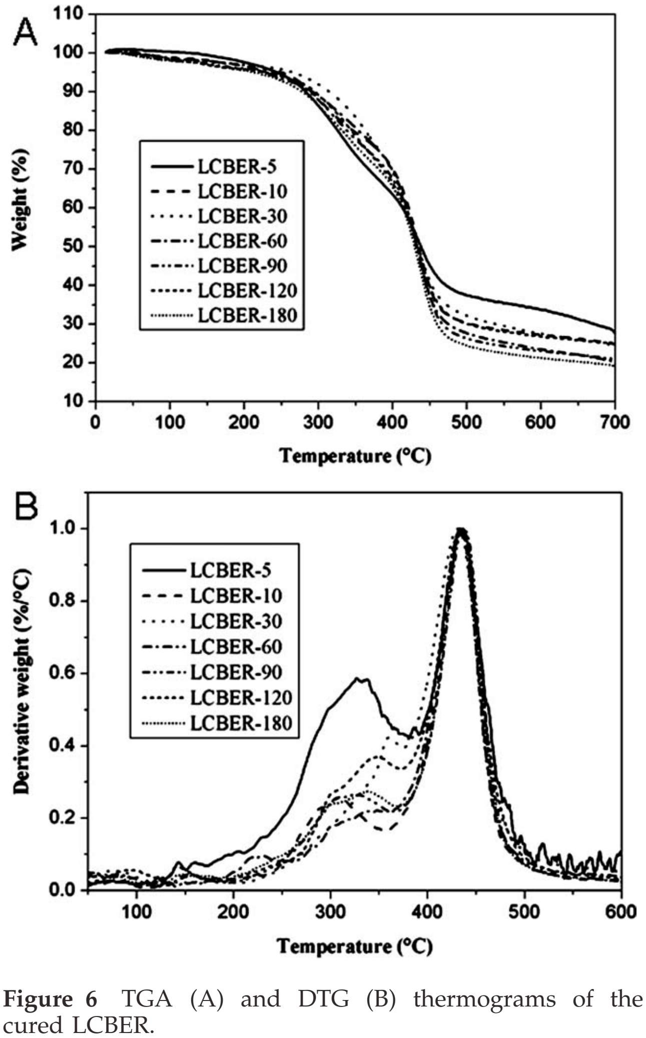


Figure 6 TGA (A) and DTG (B) thermograms of the cured LCBER.

(213.0°C) of LCBER-180 is obtained. Such increase in the T_d of the LCBER thermosets is attributed to the volume of the LCBER huge molecule from cellulose and hemi-cellulose degradation products. From Figure 3, the larger molecule LCB has the more macromolecular than the corresponding LCBER possesses, which generates a steric hindrance effect and leads to high T_d values and an increase from LCBER-5 to LCBER-30. The LCBER-180 has less huge molecule and lower T_d. However, the temperature at the rapid weight loss of the LCBER thermosets is little changed. Furthermore, it is also noticed that the char yields of the LCBER-5, LCBER-10, and LCBER-30 thermosets at 600°C are more than those of the other LCBER ones. This result indicates that LCBER-5, LCBER-10, and LCBER-30 which containing hemi-cellulose and cellulose macromolecular chain can increase the char yield significantly because of the formation of macromolecular crosslinking network during the decomposition of the LCBER. The result plays an important role to improve the flame retardancy of LCBER. It can be deduced that the formation of the macromolecular chain in the decomposition of LCBER thermosets not only increased the 5% weight loss temperature (T_d) but also resulted in a high char yield. This macromolecular char yield can limit the production of combustible carbon-containing gases, reduce the exothermicity caused by the pyrolysis reactions, and the thermal conductivity of the surface burning material, and thus, improve the flame retardancy of LCBER.

CONCLUSIONS

In this study, we successfully synthesized liquefied CB-based epoxy resins from phenol-liquefied CB biomass. The average molecular weights of LCB and LCBER and the thermodynamic properties of cured LCBER were clarified. The epoxy index became increased when the amount of BP of LCB was increased. GPC measurement demonstrated that the distribution of LCBER was changed with the corresponding LCB in various liquefaction times. The molecular weight distribution of hemi-cellulose and cellulose in CB, and the amount of epoxy group linked in them play an important role to the thermal and mechanical properties of the cured LCBER, which indicated good adhesive property and thermal stability. Furthermore, it has potential applications in biomass industry.

References

1. Fierz-David, H. E. Chem Ind Rev 1925, 44, 942.
2. Miller, I. J.; Fellows, S. K. Nature 1981, 289, 389.
3. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. J Appl Polym Sci 1994, 52, 1629.
4. Lee, S. H.; Yoshioka, M.; Shiraishi, N. J Appl Polym Sci 2002, 78, 311.
5. Tymchyshyn, M.; Xu, C. Bioresource Technol 2010, 101, 2483.
6. Ono, H.; Sudo, K. Jpn. Pat. 2,611,166 (1997).
7. Yamada, T.; Toyoda, S.; Shimize, K.; Ono, H. Jpn. Pat. 3,343,564 (2002).
8. Zhang, Y. C.; Ono, H. Bioresource Technol 2006, 97, 313.
9. Xie, T.; Chen, F. G. J Appl Polym Sci 2005, 98, 1961.
10. Yan, Y. B.; Hu, M. M.; Wang, Z. H. Bioresource Technol 2010, 32, 349.
11. Kobayashi, M.; Tukamoto, K.; Tomita, B. Holzforschung 2000, 54, 93.
12. Kobayashi, M.; Hatano, Y.; Tomita, B. Holzforschung 2001, 55, 667.
13. Asano, T.; Kobayashi, M.; Tomita, B.; Kajiyama, M. Holzforschung 2007, 61, 14.
14. Kishi, H.; Fujita, A.; Miyazaki, H.; Matsuda, S.; Murakami, A. J Appl Polym Sci 2006, 102, 2285.
15. Yamada, T.; Ono, H. Bioresource Technol 1999, 70, 61.
16. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. Wood Sci Technol 1995, 30, 39.
17. Alma, M. H.; Shiraishi, N. J Polym Eng 1998, 18, 179.
18. Demirbas, A. Energ Convers Manage 2000, 41, 633.
19. Ono, H.; Zhang, Y. C.; Yamada, T. Trans Mater Res Soc Jpn 2001, 26, 807.
20. Lin, L.; Yao, Y.; Yoshioka, M.; Shiraishi, N. Holzforschung 1997, 51, 316.
21. Schafer, A.; Seibold, S.; Walter, O.; Doring, M. Polym Degrad Stab 2008, 93, 57.
22. Yamada, T.; Ono, H. J Wood Sci 2001, 47, 458.