Macromol. Symp. **2005**, *224,* 343-353

Curing and Glass Transition of Epoxy Resins from Ester-Carboxylic Acid Derivatives of Mono- and Disaccharides, and Alcoholysis Lignin

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Summary: Mono- and disaccharides (SAC) such as glucose (Glc), fructose (Frc) and sucrose (Suc), and also alcoholysis lignin (AL) were dissolved in ethylene glycol and each of the obtained mixtures was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives such as SAC-polyacid, SACPA, and AL-polyacid, ALPA. Ethylene glycol-polyacid (EGPA) was also prepared from ethylene glycol. Each of the obtained mixtures of ester carboxylic acid derivatives was reacted with ethylene glycol diglycidyl ether in the presence of a catalytic amount of dimethylbenzylamine to form ester-epoxy resins. The molar ratios of epoxy groups to carboxylic acid groups ([EPOXY]/[ACID] ratios, mol mol^{-1}) was maintained at 1.0. The contents of SACPA and ALPA in the mixtures of SACPA/EGPA, and ALPA/EGPA, respectively, were also varied from 0 to 100 %. The curing reaction of SucPA and ALPA was studied by differential scanning calorimetry (DSC). Activation energy of the curing reaction for the SucPA system was 80.5 kJ/mol. Thermal properties of epoxy resins were studied by DSC. Glass transition temperatures (T_g) decreased with increasing numbers of repeating units in ester chains between cross-linking points, suggesting that ester chain lengths between cross-linking points mainly affect the mobility of ester chains in epoxy resin networks.

Keywords: alcoholysis lignin; curing reaction; epoxy resins; glass transition; mono- and disaccharides

Introduction

The main plant components such as cellulose, hemicellulose and lignin are recognized as the most important renewable resources, since the amount of their production is large.[1] Mono- and disaccharides such as glucose, fructose and sucrose are also abundantly produced from sugar cane and other plants.[2] Therefore, the utilization of the above plant

DOI: 10.1002/masy.200550630

components and saccharides has been extensively studied in the past. Many attempts at chemical and physical modifications of the above materials have been made in order to obtain various kinds of polymers. In the last ten years, synthetic polymers[3,4] including polyurethanes and polycaprolactones[5–9] derived from saccharides and lignin, which are the main components of plant materials, have been extensively studied by our research group.

Epoxy resins are known to be one of the important thermoset polymers, since they are used as various materials such as adhesives, composite matrices and elastomers.[10] Recently, aliphatic polyesters, such as polycaprolactones, poly(ethylene succinate) and poly(lactic acid), have received considerable attention due to the fact that they are biodegradable.[11] In our previous study, we investigated synthesis and thermal properties of the ester type of epoxy resins, which can be derived from lignin, polyethylene glycol diglycidyl ether and azelaic anhydride.[12] Other types of epoxy resins were also prepared from ester-carboxylic acid derivatives of mono- and disaccharides (SAC)[13], and alcoholysis lignin (AL).[14] In the present study, epoxy resins were prepared from ester-carboxylic acid derivatives, which were derived from SAC such as Glc, Frc and Suc, and also from AL. The curing reaction was investigated in detail by DSC. The glass transition behaviour of the obtained epoxy resins was also studied by DSC. The influence of the difference in chemical structure of epoxy resins on the curing process and glass transition is investigated.

Experimental

Materials. SAC such as Glc, Frc and Suc was commercially obtained from Wako Pure Chemical Industries, Ltd., Japan. Alcoholysis lignin (AL) was obtained from Repap Technologies, Inc., U.S.A. They were dried in vacuum at 70 °C with the presence of phosphorous pentoxide. Other reagents such as ethylene glycol (EG), glycerin (Gly), succinic anhydride (SAH), ethylene glycol diglycidyl ether (EGDGE) and dimethylbenzylamine (DMBA) were also commercially obtained from Wako Pure Chemical Industries, Ltd., Japan. The above reagents were used without further purification.

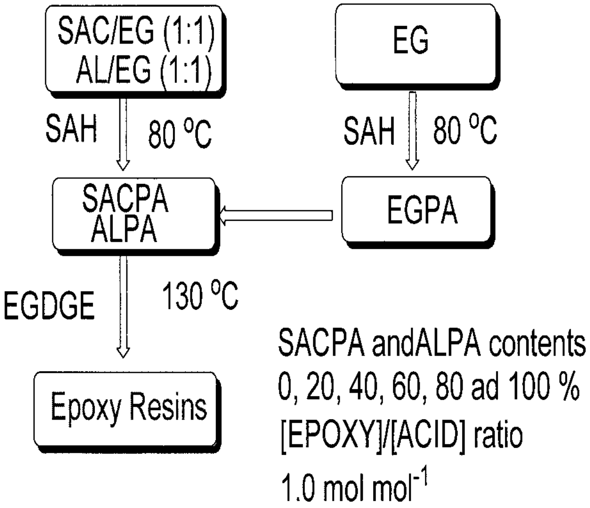
Preparation of epoxy resins. SAC and AL polyacids (SACPA and ALPA) were prepared according to the method reported previously[13,14]. Each of the SACPA and ALPA samples was mixed well with EGDGE at 80 °C, and the mixture was allowed to stand at 130 °C for 5 h in an oven. The synthetic scheme of the epoxy resins is also shown in Scheme I.

Epoxy resins were also synthesized from GlyPA in the same manner, as a reference. The molar ratios of carboxylic acid groups to the epoxy groups [EPOXY]/[ACID] ratio (mol mol^{-1}) was kept at 1.0. SACPA and ALPA contents were also varied at 0, 20, 40, 60, 80 and 100 %. The [EPOXY]/[ACID] ratios and the SACPA contents were calculated by the following equations.

$$[\mathrm{EPOXY}]/[\mathrm{ACID}] \text{ ratio (mol/mol)} = (M_{EGDGE} \mathrm{X}\ W_{EGDGE}) / (M_{SACPA} \mathrm{X}\ W_{SACPA} + M_{EGPA} \mathrm{X}\ W_{EGPA})$$

$$\text{SACPA content (\%)} = [W_{SACPA} / (W_{SACPA} + W_{EGPA})] \mathrm{X}\ 100$$

where M_{EGDGE} is the mole number of epoxy groups per gram of EGDGE (7.7 mmol g^{-1}), W_{EGDGE} the weight of EGDGE, M_{SACPA} the mole number of carboxylic acid groups per gram of SACPA (Glc 7.50, Frc 7.50 and Suc 7.35 mmol g^{-1}), W_{SACPA} the weight of SACPA, M_{EGPA} the mole number of carboxylic acid groups per gram of EGPA (7.63 mmol g^{-1}), and W_{EGPA} the weight of EGPA. The [EPOXY]/[ACID] ratios and the ALPA contents were calculated in the same manner as those for SACPA.

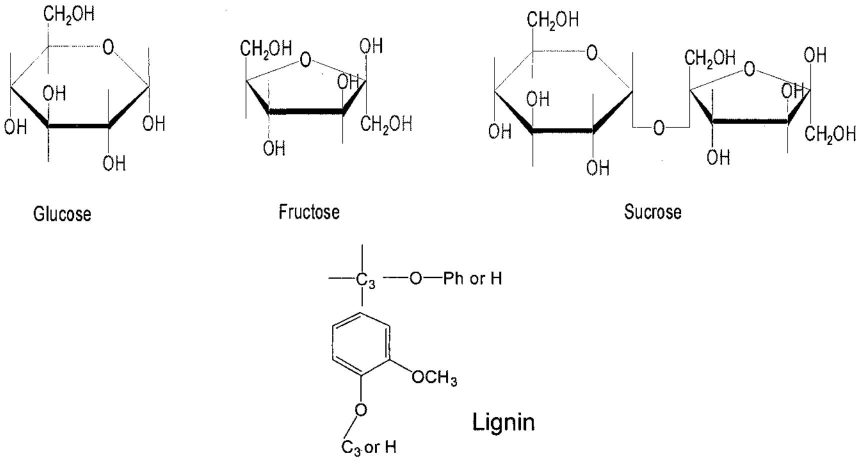


Scheme I. Preparation scheme for epoxy resins from SACPA and PLPA. Abbreviated terms in the scheme can be referred in the text in Experimental.

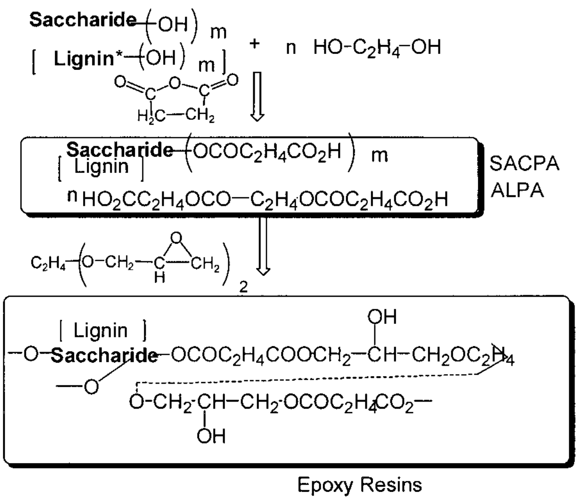
Measurements. A Perkin-Elmer Spectrum One Fourier transform infrared spectrometer was used for infrared spectrometry. The measurements were carried out using a universal ATR unit. A Seiko DSC 220 was used for differential scanning calorimetry (DSC). For the analysis of the curing reaction for SucPA and ALPA systems with 100% contents, the samples with predetermined reaction time intervals at 110 °C in an oven were cooled to room temperature. Glass transition temperatures of the above obtained samples were measured by DSC from -60 to 60 °C at a heating rate of 10 °C min^{-1}. Activation energies of curing reactions for SucPA and ALPA systems were calculating by a method reported by Ozawa[15] using DSC data with various heating rates. The measurements of the phase transition of epoxy resins after curing at 130 °C were carried out ranging from – 60 °C to 80 °C at a heating rate of 10 °C min^{-1} using ca. 5 mg of samples. The samples were heated to 130 °C and maintained for 10 min, and then they were quenched to – 60 °C in DSC aluminum vessels before measurements. The glass transition temperatures (T_g) were determined according to a method reported by Nakamura et al.[16] and Hatakeyama et al.[17]

Results and Discussion

In the present study, epoxy resins were prepared as follows. Ester-carboxylic acid derivatives of SAC and AL (the chemical structure of the above saccharides and also AL are shown in Figure 1) were obtained by the reaction with EGDGE. The reaction scheme is shown in Scheme II.



e 1. Chemical structures of saccharides and simplified schematic chemical structure nin.



Scheme II. Schematic chemical structure of epoxy resins from saccharides and lignin. Abbreviated terms in the scheme can be referred in the text in Experimental.

In our previous studies on epoxy resins from AL[14], the curing reaction was analyzed by DSC and the activation energy was calculated. However, the curing process has not been fully investigated. Therefore, in the present study, the changes in chemical structure and glass transition temperatures of epoxy resins during the curing process were studied. Figure 2 shows FTIR spectra of epoxy resins from SucPA with various curing reaction times at 110 °C. The characteristic absorption peaks of ester groups at 1730, 1200 cm^{-1}, and also that of hydroxyl groups at 3450 cm^{-1}, are observed in the spectra, and the absorbances of the above peaks increase with increasing curing reaction times when reaction times are less than 3 h.

Figure 3 shows DSC curves of epoxy resins from SucPA with various curing reaction times. It can be seen from the figure that T_g values of epoxy resins change dependently on the curing times. Figure 4 shows the change in glass transition temperatures (T_g) of epoxy resins from SucPA and ALPA with various curing reaction times. It is clearly seen that T_g values of epoxy resins from SucPA and ALPA increase with increasing curing reaction time and reach constant values when curing reaction time is ca. 3 h suggesting that the curing reaction at 110 °C is completed within 3 h and that cross-linking densities of epoxy resins reach a constant value in the reaction time region over 3 h. The above results agree

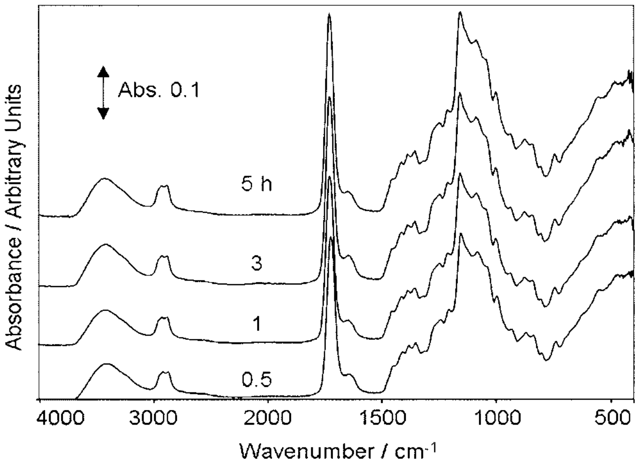


Figure 2. FTIR spectra of epoxy resins from SucPA with various reaction times.

well with the result that a DSC exothermic peak due to the curing reaction was observed within ca. 3 h in isothermal measurements at 110 °C for the above reaction system, although the results are not shown. In order to calculate the activation energy (ΔE) of curing reactions for the SucPA system, exothermic peaks were measured by DSC with various heating rates.

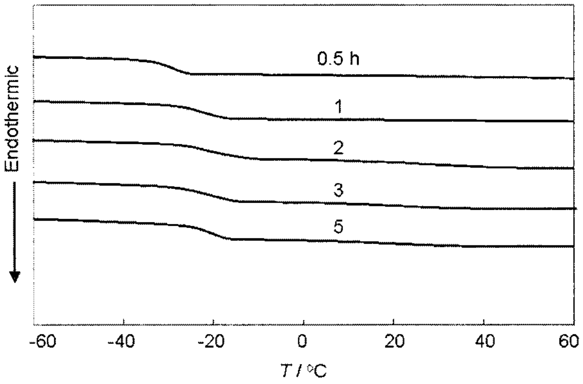


Figure 3. DSC curves of epoxy resins from SucPA with various curing reaction times.

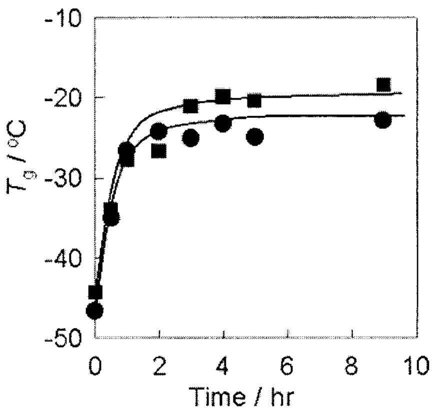


Figure 4. Changes in T_g of epoxy resins from SucPA and ALPA having 100% contents with curing reaction times. Suc (■) and AL (●).

Figure 5 shows DSC heating curves with various heating rates for the SucPA system. Using the above DSC exothermic data (heat of the curing reaction), as shown in Figure 6, logarithmic heating rates were plotted against reciprocal temperatures where a certain conversion rate is given at each heating rate. The calculated ΔE value of the curing reaction for the SucPA system, according to Ozawa's equation, was 80.5 kJ/mol. The above value is almost the same as that for the ALPA system, 83.5 kJ/mol[14]. Generally,

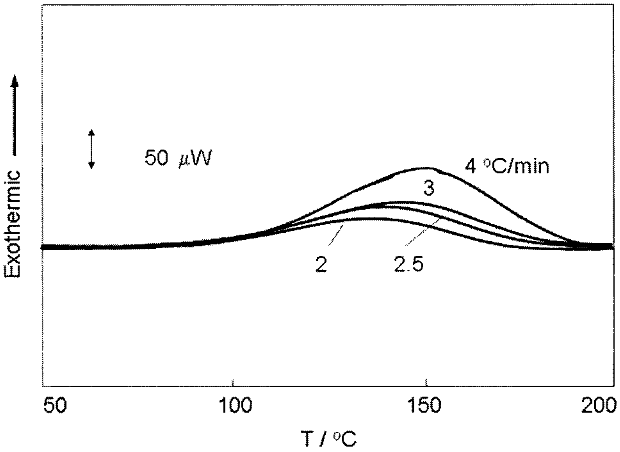


Figure 5. DSC heating curves with various heating rates for curing of the SucPA system.

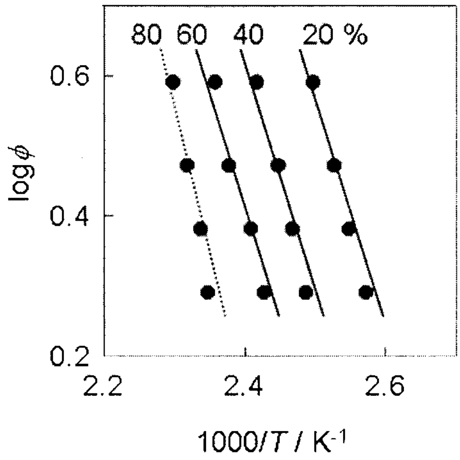


Figure 6. Plots of logarithmic heating rates and reciprocal temperatures where a certain reaction rate is given at each heating rate. Numbers indicate reaction rates in %.

the addition reaction of carboxylic acid groups to epoxy groups is affected by the nucleophilicity of carboxylate groups that is reduced by the presence of electron withdrawing substituents. Sucrose molecules have primary and secondary aliphatic hydroxyl groups, while AL molecules have primary and secondary aliphatic hydroxyl groups as well as phenolic hydroxyl groups. It is considered that the effect of the difference in chemical structures of sucrose and AL on curing reactions between epoxy groups and carboxylic groups in SucPA and ALPA molecules is negligibly small. This is because ethylene and ester groups exist between carboxylic acid groups and Suc or AL residue. Furthermore, it is observed that the calculated value of the curing reaction at a conversion rate of 80 % is 100 kJ/mol, suggesting that the curing reaction is controlled by diffusion of reaction sites in the SucPA reaction system, similarly to the ALPA reaction system[13].

The phase transition of epoxy resins was studied by DSC. Figure 7 shows the changes of T_g against the SACPA and ALPA content of epoxy resins. T_g increases with increasing SACP and ALPA contents, while ΔC_p decreases with increasing SACPA and ALPA contents of epoxy resins, although ΔC_p's are not shown in the figure. The above results indicate that saccharides and lignin act as hard segments in epoxy resin molecules. It is considered that saccharides and lignin exist as cross-linking points and that the chain

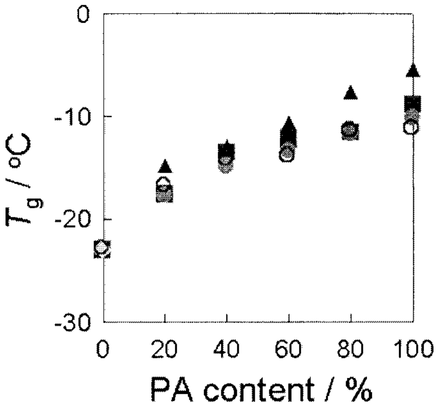


Figure 7. Changes in T_g's with SACPA and ALPA contents of epoxy resins. Glc (■), Frc (●), Suc (▲) and AL (○).

lengths of epoxy resins between cross-linking points decrease with increasing SACPA and ALPA contents in epoxy resins.

Figure 8 shows the relationship between T_g and the calculated number of repeating units (one unit consists of EGPA 1 mol and EGDGE 1 mol) between cross-linking points. The increase in the chain lengths between cross-linking points enhances the main chain molecular motion.

Furthermore, T_g values of epoxy resins from Suc are always higher than those from other components, particularly in the high SACPA content region. The above results suggest that the effect of the chemical structure of saccharides on the main chain motion of epoxy resins between cross-linking points becomes prominent particularly in the higher SACPA content region. The results of epoxy resins from glycerin (Gly) are also shown in Figure 8, as a reference. The T_g values of epoxy resins from Glc, Frc and Gly are almost the same, suggesting that the effects of ring structure on the main chain motion of epoxy resins are low in the present epoxy resin system, particularly in the region of high numbers of repeating units, i.e. in the small saccharides contents region. In the case of epoxy resins from AL, the T_g values are similar to those from saccharides in the area of the high values of the number of repeating units, suggesting that the effect of the cross-linking components is limited when the number of repeating units between cross-linking points is

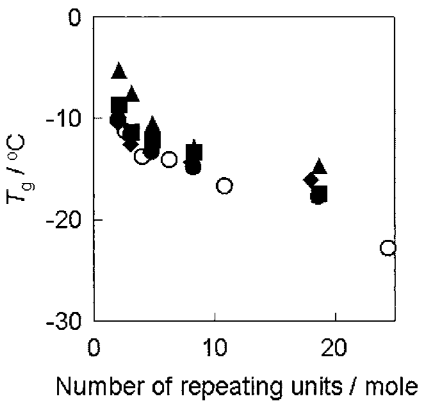


Figure 8. Relationship between T_g's and calculated number of repeating units between cross-linking points for epoxy resins from SACPA and ALPA. Glc (■), Frc (●) and Suc (▲), Gly (♦) and AL(○).

sufficiently high. It is considered difficult to compare directly glass transition behaviour of epoxy resins with components such as saccharides and lignin having quite different chemical structures, in the region of low numbers of repeating units. This is because the higher order structures of epoxy resin molecules having saccharides or lignin with aliphatic ester chains are strongly affected by the molecular interaction of the above components in molecules of the present epoxy resin system.

Conclusions

Epoxy resins were prepared by the reaction of the ester-carboxylic acid derivatives with EGDGE in the presence of a catalytic amount of BMBA at [EPOXY]/ [ACID] ratio 1.0. The curing process of SACPA and ALPA was studied by DSC. DSC results suggest that the curing process proceeds in the same manner in SACPA and ALPA systems. The T_g increased with increasing SACPA and ALPA contents in epoxy resins, suggesting that saccharides and lignin act as cross-linking agents in epoxy resins.

[1] K. Kringstad, in "*Future Sources of Organic Raw Materials – CHEMRAWN* I", (L. E. St. Pierre et al., Eds.), Pergamon Press, 1980, p. 627.
[2] F. W. Lichtenthaler and S. Mondel, *Pure & Appl. Chem.*, **1997**, *69*, 1853.
[3] H. Hatakeyama, S. Hirose, T. Hatakeyama, K. Nakamura, K. Kobashigawa, N. Morohoshi, *J. Macromol. Sci.*, **1995**, *A32*, 743.
[4] H. Hatakeyama, *J. Therm. Anal. Calorimetry*, **2002**, *70*, 755.
[5] S. Hirose, K.Kobashigawa, H. Hatakeyama, *Sen'i Gakkaishi*, **1994**, *50*, 538.
[6] N. Morohoshi, S. Koh, H. Hatakeyama, S. Hirose, *Sen'i Gakkaishi*, **1994**, *50*, 143.
[7] P. Zetterlund, A. –C. Albertsson, S. Hirose, T. Hatakeyama, H. Hatakeyama, *Polym. Intl.*, **1997**, *32*, 1.
[8] H. Hatakeyama, K. Kobashigawa, S. Hirose, T. Hatakeyama, *Macromol. Symp.*, **1998**, *130*, 127.
[9] H. Hatakeyama, Y. Izuta, S. Hirose, T. Yoshida, T. Hatakeyama, in "*Recent Advances in Environmentally Compatible Polymers*", J. F. Kennedy, P. A. Williams, G. O. Phillips, H. Hatakeyama Eds., Woodhead Publisher Ltd., Chichester, 2001, p. 33.
[10] M. S. Bhatnagar, in "*Polymeric Materials Encyclopedia*" (J. C. Salamone ed.), CRC Press, New York, 1996, p.2233.
[11] A. -C. Albertsson and I. K. Varma, in "*Advances in Polymer Science, 157 (Degradable Aliphatic Polyesters)*", Springer-Verlag, 2002, p. 1.
[12] S. Hirose, M. Kobayashi, H. Kimura, H. Hatakeyama, in "*Recent Advances in Environmentally Compatible Polymers,*" J. F. Kennedy, P. A. Williams, G. O. Phillips, H. Hatakeyama Eds., Woodhead Publisher Ltd., Chichester, 2001, p.73.
[13] S. Hirose, T. Hatakeyama, H. Hatakeyama, *Netsu Sokutei*, **2003**, *30*, 154.
[14] S. Hirose, T. Hatakeyama, H. Hatakeyama, *Macromol. Symp*, **2003**, *197*, 157.
[15] T. Ozawa, *Bull. Chem. Soc., Japan*, **1965**, *38*, 1881.
[16] S. Nakamura, M. Todoki, K. Nakamura, H. Kanetsuna, *Thermochimica Acta* **1988**, *163*, 136.
[17] T. Hatakeyama, F. X. Quinn, "*Thermal Analysis*", John-Wiley & Sons Ltd., Chichester, 1994, p.38/64.