

# Synthesis and Thermal Properties of Epoxy Resins Cured with Lignin-related Biphenols Having Syringyl Structure

Shigeo HIROSE, Yusuke SAKAMOTO and Yoshihiko SUGAMORI

Faculty of Engineering, Department of Environmental and Biological Chemistry

4,4'-Dihydroxy-3,3',5,5'-teramethoxybiphenyl (DHTMB) was synthesized from syringol, which can be obtained by thermal and hydration degradation of lignin. As the model reaction for curing, octaethylene glycol diglycidyl ether was cured with DHTMB and also with 4,4'-dihydroxybiphenyl (DHB) in the presence of 2-ethyl-4-methylimidazole (2E4MI). Curing reaction was studied by differential scanning calorimetry (DSC). The calculated activation energies ( $E_a$ 's) were almost the same values for both curing systems. The mixture of epoxy compounds consisting of trimethylolpropane triglycidyl ether and diethylene glycol diglycidyl ether was cured with DHTMB in the presence of 2E4MI. The above mixture of epoxy compounds was also cured with DHB. Thermal properties of cured epoxy resins were investigated by DSC. Glass transition temperature determined by DSC was 46.6 °C for that cured with DHTMB and 38.8 °C for that with DHB, suggesting that the existence of bulky methoxyl groups in syringyl structure restricts the main chain motion of cured epoxy resin.

**Key Words :** Lignin-related Phenols, Biphenols, Syringyl Groups, Curing Agent, Curing Reaction, Glass Transition Temperature

## 1. Introduction

Plant biomass has attracted considerable attention, since it can be produced in large quantities, is renewable, and also provides circulation of carbon in the ecological system<sup>(1)</sup>. The concept "Biorefinery" has been developed rapidly in order to establish sustainable chemical industries<sup>(2)</sup>.

Epoxy resins are known to be one of the most important network polymers, since they are used in a wide range of industrial fields as materials such as adhesives, composites and elastomers<sup>(3)</sup>. Many researchers have studied ether-type lignin-based epoxy resins<sup>(4,5)</sup>. Malutan et al. reported epoxy resins which were derived from hydroxymethylated lignin<sup>(6)</sup>.

Our research group has developed various new highly functional and high performance polymers, which can be derived from biomass components such as saccharides, polysaccharides, lignin, and vegetable oil components. Hatakeyama et al. have extensively studied various types of polyurethanes including composites<sup>(7-9)</sup>. Recently, new types of epoxy resins with polyester chains, which can be derived from saccharides, lignin and glycerol have been studied<sup>(10-14)</sup>. In the above studies, the relationship between chemical structure and physical properties was investigated<sup>(15)</sup>. It is known that phenols having the characteristic chemical structures such as 4-hydroxyphenyl, 4-hydroxy-3-methoxyphenyl (guaiacyl) and 4-hydroxy-3,5-dimethoxyphenyl (syringyl) structure can be obtained by the degradation of lignin<sup>(12)</sup>. We have previously reported that liquid crystalline polyesters were obtained from biphenol with syringyl structure<sup>(16)</sup>. In the present study, novel cured epoxy resins were derived from a biphenol derivative with syringyl structure and aliphatic epoxy compounds, in order to study the basic elements for molecular design for the research on the high performance cured epoxy resins. The influence of methoxyl groups in syringyl structure on the reactivity of hydroxyl groups with epoxy groups and on the main chain

\* 原稿受付 2016 年 2 月 26 日

\*1 工学部 環境生命化学科

E-mail: s-hirose@fukui-ut.ac.jp

motion of cured epoxy resins molecules were investigated.

## 2. Experiment

### 2.1 Materials

Syringol, PbO<sub>2</sub>, hydrazine monohydrate, 4,4'-dihydroxybiphenyl and 2-ethyl-4-methylimidazole were commercially obtained from Wako Chemical Industries. Trimethylpropane triglycidyl ether was commercially obtained from Aldrich-Sigma Co. Ltd. Octaethylene glycol diglycidyl ether and diethylene glycol diglycidyl ether were kindly supplied by Sakamoto Chemical Industries Co. Ltd., Japan. Each reagent was used for experiment without further purification.

### 2.2 Synthesis

#### 2.2.1 Synthesis of 4,4'-dihydroxy-3,3',5,5'-teramethoxybiphenyl (DHTMB)

4,4'-Dihydroxy-3,3',5,5'-teramethoxybiphenyl (DHTMB) was synthesized according to a method reported previously<sup>(16)</sup>. 3,3'-5,5'-Diphenoquinone was synthesized by the oxidative coupling of syringol using PbO<sub>2</sub>. DHTMB was obtained by the reduction of the diphenoquinone derivative by hydrazine. The obtained crude product was purified by recrystallization from a mixed solvent consisting of toluene and ethanol followed by vacuum distillation using a glass tube oven distillator. The compound was identified by mp. 194-195 °C (*lit.* 194-195 °C)<sup>(16)</sup>, FTIR and NMR spectra.

#### 2.2.2 Model reaction of curing

Octaethylene glycol diglycidyl ether (OEGDGE) and DHTMB were placed in a flask. A catalytic amount of 2-ethyl-4-methylimidazole (2E4MI) was added to the reaction mixture. The [EPOXY] / [OH] (mol/mol) ratio was 1.0. The reaction mixture was stirred and heated at 120 °C for 40 min in vacuum. The obtained prepolymer solution was cured during heating from 25 to 200 °C in a sample vessel of differential scanning calorimetry (DSC). The model reaction using 4,4'-dihydroxybiphenyl (DHB) was also carried out in the same manner.

#### 2.2.3 Synthesis of cured epoxy resins

DHTMB and a mixture of epoxy compounds consisting of trimethylpropane triglycidyl ether (TMPTGE) and diethylene glycol diglycidyl ether (DEGDGE) were placed in a flask. A catalytic amount of 2-ethyl-4-methylimidazole (2E4MI) was added to the reaction mixture. The mole ratio of TMPTGE to DEGDGE was 1:1. The [EPOXY] / [OH] (mol/mol) ratio was 1.0. The reaction mixture was stirred and heated at 80 °C for 4 h in vacuum. The obtained prepolymer solution was cured at 130 °C for 5 h in an oven. The cured epoxy resin was also prepared from DHB in the same manner.

### 2.3 Measurement

A Seiko DSC 220 was used for differential scanning calorimetry (DSC). The measurements of curing reaction were carried out from 25 to 200 °C, at heating rates of 1.25, 1.50, 1.75 and 2.00 °C/min. The activation energies were determined using Ozawa's method<sup>(17)</sup>. The measurements of glass transition of epoxy resins were carried out at temperature ranging from -70 °C to 80 °C at a heating rate of 10 °C/min using ca. 5 mg of samples. The samples were heated at 130 °C and maintained for 10 min., and then were quenched to -70 °C in DSC aluminium vessels before measurements. The glass transition temperature ( $T_g$ ) was determined according to a reported method<sup>(18)</sup>. A Perkin-Elmer Spectrum One Fourier transform infrared spectrometer (FT-IR) equipped with a universal ATR unit was used to analyze the functional groups. A JEOL Datum JNM-ATUM FTNMR spectrometer was used for the determination of chemical structure of DHTMB.

## 3. Results and Discussion

### 3.1 Model reaction of curing

The model reaction of curing was carried out using OEGDGE as an epoxy compound when biphenols such as DHTMB and DHB were used as curing agents. In the above model reactions, 2-ethyl-4-methylimidazole (2E4MI) was used as an accelerator. Fig. 1 shows the reaction scheme of model reaction. The precise procedure is described in the experimental session.

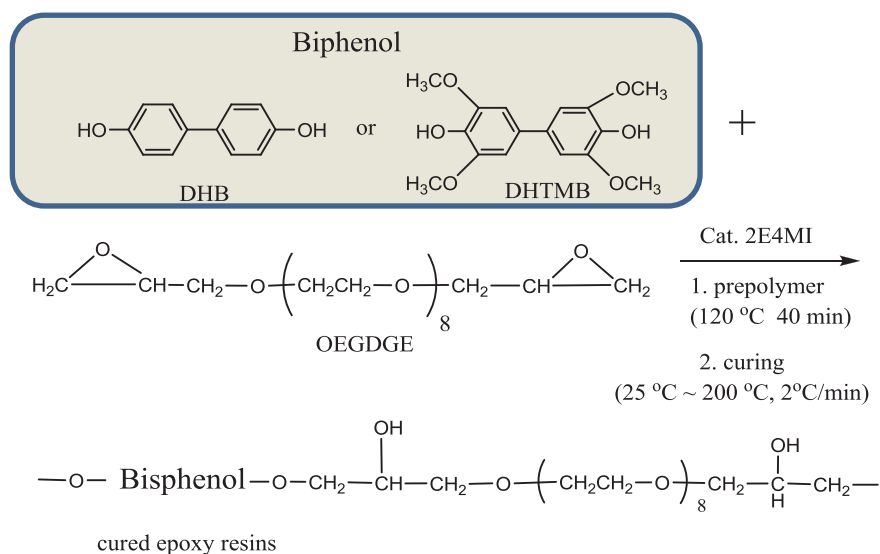


Fig. 1 Reaction scheme of model reaction of curing.

Fig. 2 shows FTIR spectra of the prepolymer of both before and after heating up to 200 °C, for both systems using DHTMB. After heating prepolymers up to 200 °C, the absorption peak at ca. 910 cm<sup>-1</sup> for epoxy groups are not observed and that at ca. 3400 cm<sup>-1</sup> for hydroxyl groups shows a change in the absorption value in FTIR spectra for both DHTMB and DHB systems. The above results indicate that curing reaction of epoxy groups with phenolic hydroxyl groups proceeds as expected.

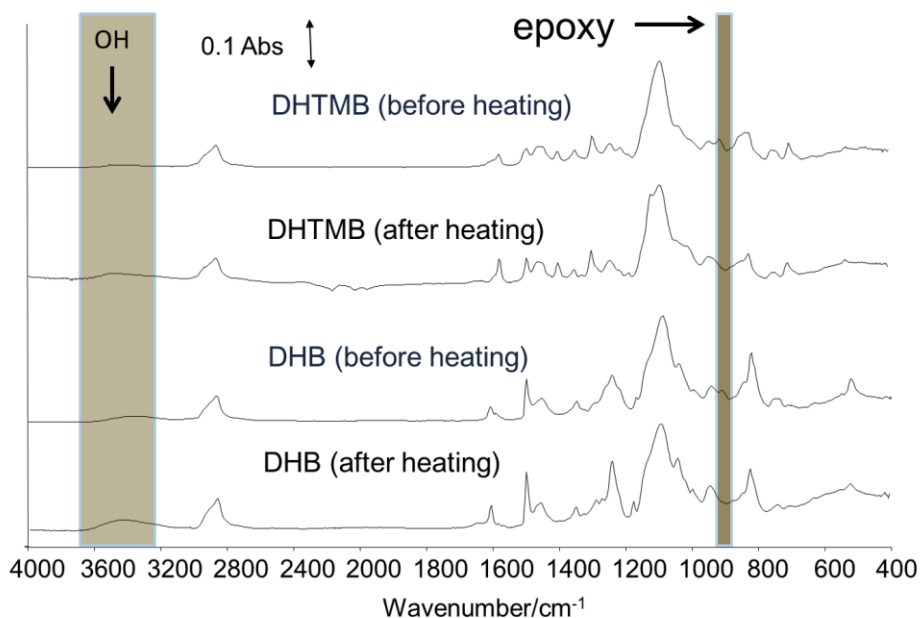


Fig. 2 FTIR spectra of prepolymers before and after heating up to 200 °C for DHTMB and DHB systems.

In order to calculate activation energies ( $E$ 's) for curing reaction of DHTMB and DHB systems, DSC measurement with various heating rates were carried out. Fig. 3 shows DSC heating curves measured at heating rates of 1.25, 1.50, 1.75 and 2.00 °C/min for DHTMB system. An exothermic peak due to the curing reaction is observed in each DSC curve.

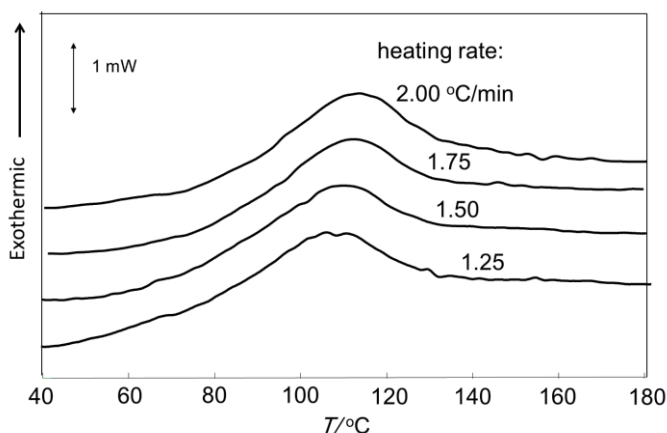


Fig. 3 DSC heating curves with various heating rates for DHTMB system.

Fig. 4 shows Ozawa's plot for DHTMB system.  $E$  value can be calculated from the tangent of each linear line. The calculated value for DHTMB system was 43 to 92 kJ/mol, and for DHB system 55 to 76 kJ/mol, respectively. The values of  $E$ 's are similar for both systems below 60% of reaction rates. It is generally known that phenols having lower values of  $pK_a$  have higher reactivity with epoxy groups<sup>(19)</sup>. Therefore, the above results seem reasonable when the fact that  $pK_a$  value of syringol (2,6-dimethoxyphenol) is 9.98 and that of phenol is 10.0 is taken into consideration<sup>(20)</sup>. However,  $E$  value for DHTMB systems is much higher than that for DHB system at 80% of reaction rate. These results suggest that the reaction mechanism may change markedly due to the existence of methoxyl groups in molecules in the reaction rate region of 80 % for DHTMB system.

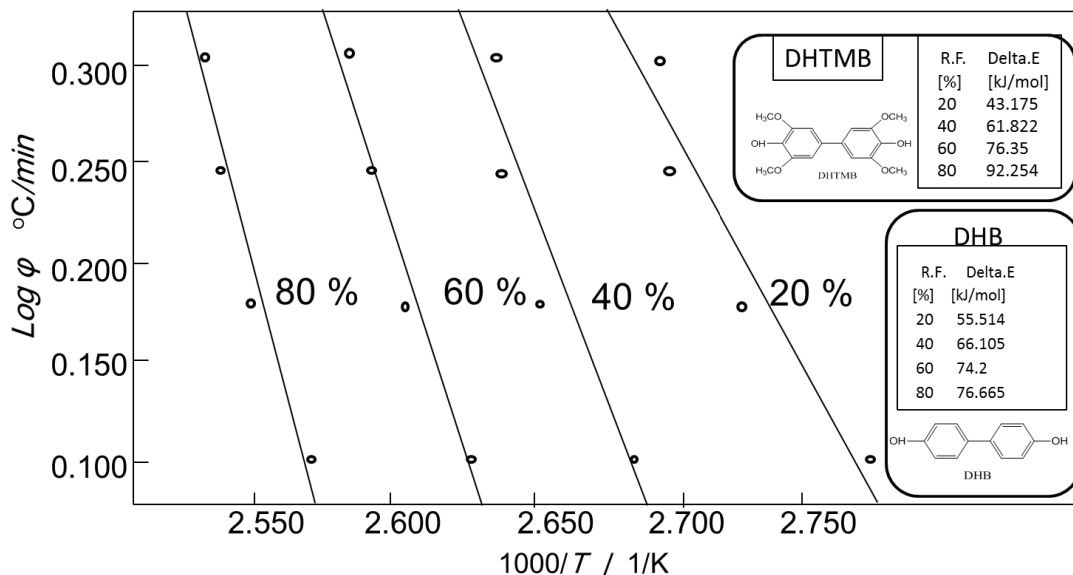


Fig. 4 Ozawa's plot for DHTMB system.

The numbers indicate the rates of the curing reaction. The  $E$  values for DHB system are also shown in the figure.

### 3.2 Cured epoxy resins with three dimensional polymer networks

In order to synthesize cured epoxy resins with network structure, the mixture of epoxy compounds consisting of trimethylopropane triglycidyl ether (TMPTGE) and diethylene glycol diglycidyl ether (DEGDGE) was used as epoxy compounds. The mole ratio of TMPTGE to DEGDGE was kept at 1.0 and also [EPOXY] / [OH] ratio (mol/mol) was 1.0. After preparing prepolymers, prepolymers were heated in DSC sample vessels up to 200 °C. Fig. 5 shows DSC heating curves for DHTMB and DHB prepolymer systems. Each DSC curve shows an exothermic peak at ca. 100 °C. Accordingly, the cured epoxy resins were synthesized by heating prepolymers at 130 °C for 5h in an oven.

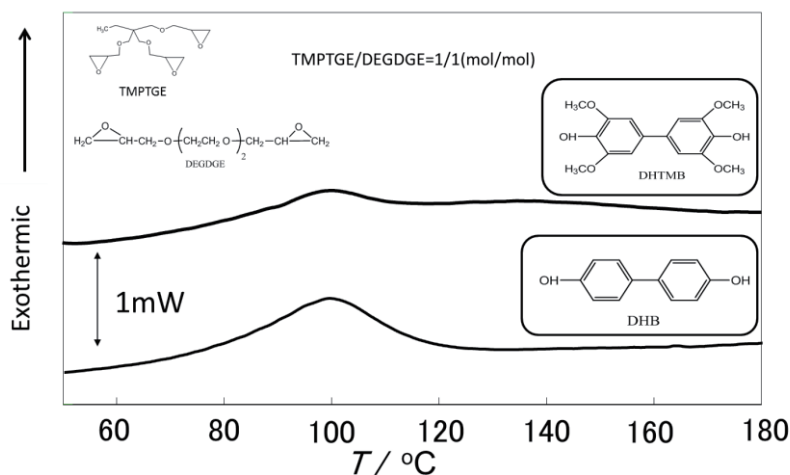


Fig. 5 DSC heating curves of curing for prepolymers of DHTMB and DHB systems.

Fig. 6 shows DSC curves of cured epoxy resins of DHTMB and DHB systems. The typical base-line gap due to glass transition is observed in each DSC curve. The determined glass transition temperature ( $T_g$ ) values are 46.4 °C for DHTMB system and 38.8 °C for DHB system, respectively. This result suggests that bulky methoxyl groups attached at ortho positions restrict the main chain motion of cured epoxy resins of DHTMB system.

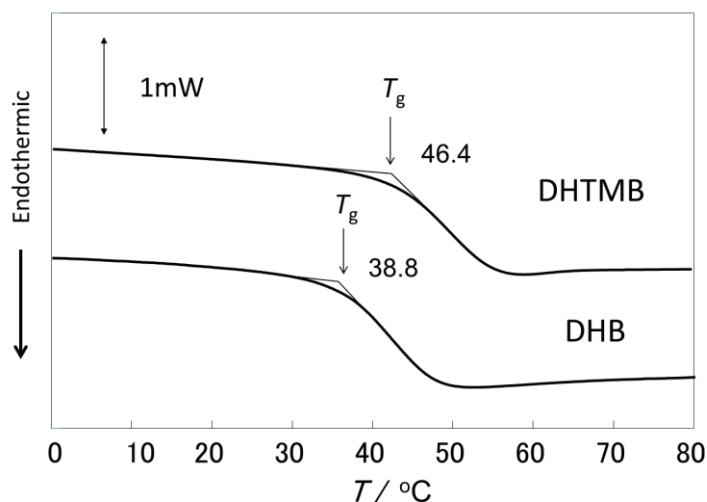


Fig. 6 DSC curves of cured epoxy resins for DHTMB and DHB systems.  
Heating rate: 10 °C/min.

#### 4. Conclusion

The calculated values of E for both DHTMB and DHB systems were almost the same in the reaction rate region below 60 %. However, the E value for DHTMB system showed a higher value than that for DHB system. The exothermic peaks due to curing reaction were observed in a similar temperature region in DSC heating curves for both DHTMB and DHB systems.  $T_g$  value of cured epoxy resins for DHTMB system was 46.6 °C and that for DHB system 38.8 °C, suggesting that bulky methoxyl groups restrict the main chain motion of cured epoxy resins molecules in the DHTMB system. The present research provided basic information for the molecular design of high performance resins using biphenols, which are derived from lignin-related phenols, as curing agents.

#### References

- [1] R. Uber, K. Maffler, N. Tippkötter, T. Hirth and D. Sell, *Renewable Raw Materials: New Feedstocks for the Chemical Industry*, R. Uber, D. Sell and T. Hirth, editors. (2011) Chapter 1, Wiley-VCH Inc.
- [2] A. Kazmi and J. Clark, *Renewable Raw Materials: New Feedstocks for the Chemical Industry*, R. Uber, D. Sell and T. Hirth (eds.), (2011), Chapter 6, Wiley-VCH Inc.
- [3] J-P. Pascault and R. J. J. Williams, "General concepts about epoxy polymers". *Epoxy polymers*, J-P. Pascault and R. J. J. Williams (eds.) (2010), p. 1-12, Wiley-VCH.
- [4] D. Feldman and D. Banu, *J. Polym. Sci. Part A: Polym. Chem.*, Vol. 26, (1987) pp. 973-983.
- [5] K. Hofmann and W. Glasser, *Macromol. Chem.*, Vol. 195 (1994), pp. 65-80.
- [6] T. Malutan, R. Nicu and V. I. Popa, *Bioresources*, Vol. 3, (2008), pp. 1371-1376.
- [7] T. Hatakeyama and H. Hatakeyama, *Thermal properties of green polymers and biocomposites* (2004), Kluwer Academic.
- [8] H. Hatakeyama, T. Nanbo and T. Hatakeyama, "Thermal and mechanical analysis of lignocellulose-based biocomposites", *Characterization of lignocellulosic materials*, T.Q. Hu (ed.) (2008), Blackwell, pp. 275-287.
- [9] H. Hatakeyama and T. Hatakeyama, "*Green Polyurethanes and Biocomposites: Molecular Design and Characterization*", (2015), Nova Science Pub Inc,
- [10] S. Hirose, M. Kobayashi, H. Kimura and H. Hatakeyama, Synthesis of lignin-based polyester-epoxy resins. *Recent advances in environmentally compatible polymers*. J. F. Kennedy, G. O. Phillips, P. A. Williams and H. Hatakeyama (eds.), (2001), p. 73-78, Woodhead.
- [11] S. Hirose, T. Hatakeyama and H. Hatakeyama, *Macromol. Symp.*, Vol. 197, (2003), p. 157-169.
- [12] S. Hirose and H. Hatakeyama, "Utilization of lignin as polymers (1)", *Fine Chemical*, CMC Publisher, Vol. 41, No. 5, (2012), p.10-16. (in Japanese)
- [13] S. Hirose, T. Hatakeyama and H. Hatakeyama, "Novel epoxy resins derived from biomass components", *Procedia Chemistry*, (S. Hirose and E. D. R. Putra eds.), Vol. 4, (2012), pp. 26-33.
- [14] S. Hirose, "Novel Epoxy Resins with Unsaturated Ester Chains Derived from Sodium Lignosulfonate", *Macromol. Symp.*, Vol. 353, (2016), pp. 31-38.
- [15] S. Hirose and H. Hatakeyama, "Curing and glass transition of epoxy resins from ester-carboxylic acid derivatives of mono- and disaccharides, and alcoholysis lignin", *Macromol Symp*, Vol. 224, (2005), pp. 343-353.
- [16] S. Hirose, M. Acevedo and H. Hatakeyama, *Prog. Polym. Phys. Japan*. Vol. 141, (1994), pp. 37 -38.
- [17] T. Ozawa, *Bull. Chem. Soc. Japan*, Vol. 38, (1965), pp. 1881-1886.
- [18] T. Hatakeyama, F. X. Quinn, *Thermal Analysis: Fundamentals and Applications to Polymer Science*, 2nd Edition, (1999), Wiley.
- [19] "*Epoxy Resins*", Vol. 1, (2003), Japan Society of Epoxy Resin Technology. (in Japanese)
- [20] M. Ragnar, C. T. Lindgren and N.-O. Nilvebrant "pKa-values of Guaiacyl and Syringyl Phenols Related to Lignin", *J. Wood Chem. Technol.*, Vol. 20, (2000), pp.277-305.

(平成 28 年 3 月 31 日受理)