

Thermal Properties of Epoxy Resins from Lignin and Lignin-related Phenols

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ABSTRACT

Epoxy prepolymers were synthesized from alcoholysis lignin (AL) and lignin-related phenols such as *p*-hydroquinone (HQ) and methoxy-*p*-hydroquinone (MHQ) by reaction with epichlorohydrin. Epoxy resins were synthesized from the above prepolymers by reaction with poly(azelaic anhydride). The molar ratios of acid anhydride groups to epoxy groups ([AA/EPOXY] ratios) were varied at 10/10 and 12/10. The thermal properties of the obtained prepolymers and epoxy resins were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG- Fourier transform infrared spectroscopy (FTIR). The values at glass transition temperatures (T_g 's) of epoxy resins decreased in the order of epoxy resins from HQ > AL > MHQ. Thermal degradation temperatures (T_d 's) of epoxy resins were almost constant regardless of [AA/EPOXY] ratios, suggesting that the curing of prepolymers with poly(azelaic anhydride) does not affect T_d values. The intensities of absorption peaks at 2900 cm⁻¹ (CH) and 1730 cm⁻¹ (C=O) in IR spectra of the evolved gases during thermal degradation increased with increasing [AA/EPOXY] ratios.

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1. INTRODUCTION

Biodegradable polyurethanes derived from lignin [1,2] and high-performance polyesters and polyethers derived from lignin-related phenols [3,4] have been extensively studied by our research group. The above polymers showed excellent thermal and mechanical properties. Many researchers have reported epoxy resins which can be derived from lignin-based epoxy-prepolymers [5-7]. In the above reaction systems, lignin-based epoxy prepolymers were cured with amines and also with aromatic anhydrides. Recently, it is reported that aliphatic polyesters are biodegradable. It is expected that epoxy resins would be biodegradable if the aliphatic ester structure could be introduced into the molecular networks of epoxy resins. Therefore, in the present study, epoxy prepolymers were synthesized from alcoholysis lignin (AL) and lignin-related phenols. Epoxy resins were synthesized from the above prepolymers by the reaction with poly(azelaic anhydride). The thermal properties of the obtained epoxy resins were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-Fourier transform infrared spectroscopy (FTIR).

2. EXPERIMENTAL

2.1 Materials

Alcoholysis lignin (AL) was kindly supplied by Repap Technologies Inc., U. S. A. Poly(azelaic anhydride) (PAA) was also kindly supplied by ICA Japan Ltd. *p*-Hydroquinone (HQ), methoxy-*p*-hydroquinone (MHQ) and epichlorohydrin (ECH) were commercially obtained from Wako Chemical Industries Ltd., Japan. All the materials were used without further purification.

Epoxy resins were synthesized by the following procedure. AL and

epichlorohydrin were reacted in a NaOH aqueous solution at 100 °C for 5 hr. The obtained precipitate of prepolymer was separated and washed with water. The precipitate was dried in air and then in an oven in vacuum at 100 °C for 24 hr. Epoxy prepolymers were also synthesized from HQ and MHQ. The prepolymers were cured with poly(azelaic anhydride) in the presence of a catalytic amount of N,N-dimethyl-p-aminophenol in N,N-dimethylformamide (DMF). The molar ratios of epoxy groups to acid anhydride groups ([AA]/[EPOXY] ratios) were varied at 10/10 and 12/10.

2.2 Measurements

DSC was carried out using a Seiko 220 DSC at a heating rate of 10 °C/min under a nitrogen flow. TG was carried out in nitrogen using a Seiko TG/DTA 220 at a heating rate of 10 °C/min. TG-FTIR was performed using a Seiko TG 220 - JASCO FTIR-420 system at a heating rate of 20 °C/min at a nitrogen flow of 200 ml/min.

3. RESULTS AND DISCUSSION

Phase transition of the obtained epoxy resins was studied by DSC. Fig. 1 shows DSC curves of epoxy resins from AL, HQ and MHQ with [AA/EPOXY] ratio 10/10. A marked change in baseline due to glass transition was observed in a DSC curve of each sample. As shown in Fig, 1, temperature range of glass transition for epoxy resin from AL is broader than those for epoxy resins from HQ and MHQ, suggesting that the distribution of units of main chain motion in epoxy resin from AL is wider than that in epoxy resins from HQ and MHQ. T_g values of epoxy resins are 0, -20 and -31 °C for the epoxy resins from HQ, AL and MHQ, respectively. It has already been reported that polyesters having methoxyphenyl groups in the main chain shows lower T_g values than those

for polyesters having phenyl groups [8]. It is considered that the existence of bulky methoxyl groups attached asymmetrically on phenyl groups enhance the main chain motion i.e. reduce the T_g value.

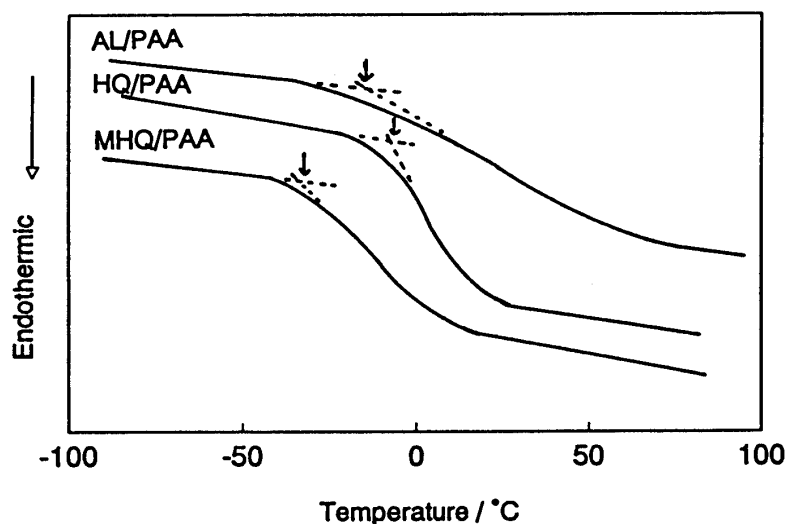


Fig. 1 DSC curves of epoxy resins from AL, HQ and MHQ with [AA/EPOXY] ratio 10/10.

The thermal degradation of epoxy resins was studied by TG and TG-FTIR. Thermal degradation temperatures (T_d 's) of prepolymers and epoxy resins were determined using TG curves. Fig. 2 shows TG curve of epoxy resin from AL with [AA/EPOXY] ratio 10/10. As shown in Fig. 2, thermal degradation apparently proceed in one step. Fig. 3 shows the relationship between [AA]/[EPOXY] ratio and T_d for prepolymers ([AA]/[EPOXY] ratio = 0/10) and epoxy resins. T_d 's of epoxy resins are almost constant regardless of [AA]/[EPOXY] ratios, suggesting that the curing of prepolymers with PAA does not affect T_d values. The values of T_d 's of prepolymers and epoxy resins are in the order of materials from HQ > MHQ > AL. These results are seasonable when we consider the fact that lignin is relatively thermally unstable. Fig. 4 shows the relationship between [AA]/[EPOXY] ratio and weight residue at 500 °C (WR). WR values decrease with increasing [AA]/[EPOXY] ratios. It is

considered that aromatic rings in epoxy resin molecules cause condensation reactions and produced non-volatile compounds during heating.

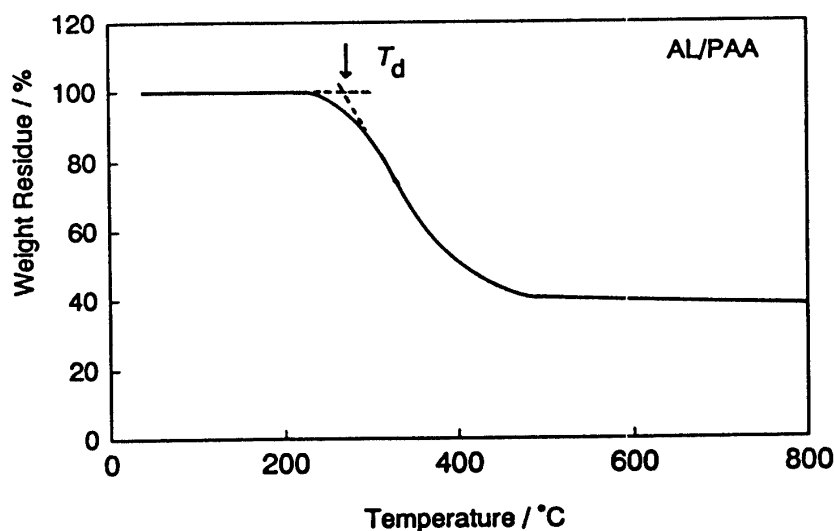


Fig. 2 TG curve of epoxy resin from AL with [AA/EPOXY] ratio 10/10.

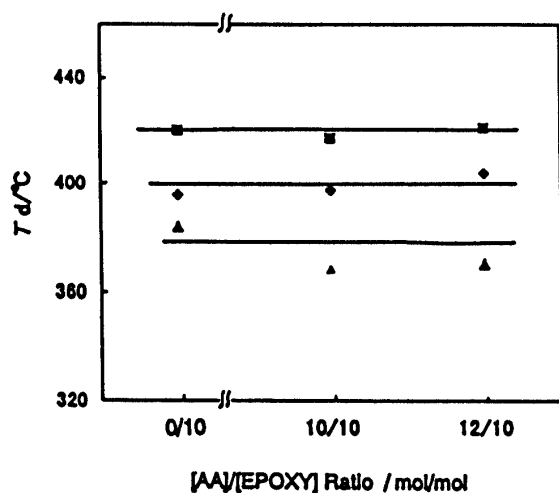


Fig.3 Relationship between [AA/EPOXY] ratio and thermal degradation temperature (T_d) of prepolymers and epoxy resins. (Δ) AL, (\blacksquare) HQ and (\blacklozenge) MHQ.

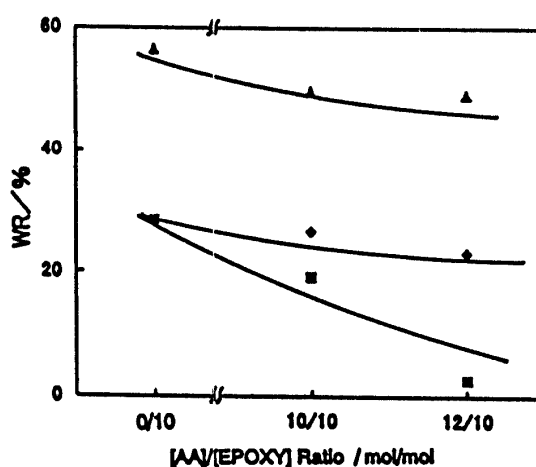


Fig. 4 Relationship between [AA/EPOXY] ratio and weight residue (WR) of prepolymers and epoxy resins. (Δ) AL, (\blacksquare) HQ and (\blacklozenge) MHQ.

The evolve gases during thermal degradation were analyzed by TG-FTIR. Fig. 5 shows stacked IR spectra of the evolved gases for the epoxy

resin from HQ with [AA]/[EPOXY] ratio 12/10. IR spectra were analyzed for evolved gases at temperatures where degradation rates show maximum values in differential TG curves. Fig. 6 shows the IR spectrum of evolved gases at 400 °C. Figs. 7 and 8 shows the relationship between [AA/EPOXY] ratio and peak intensity at 2900 cm^{-1} and 1730 cm^{-1} , respectively. It was found that the intensities of absorption peaks at 2900 cm^{-1} (CH) and 1730 cm^{-1} (C=O) increase with increasing [AA]/[EPOXY] ratios. The above results suggest that the amount of the compounds having CH and C=O groups increase with increasing the amount of azelaic acid ester groups in epoxy resins.

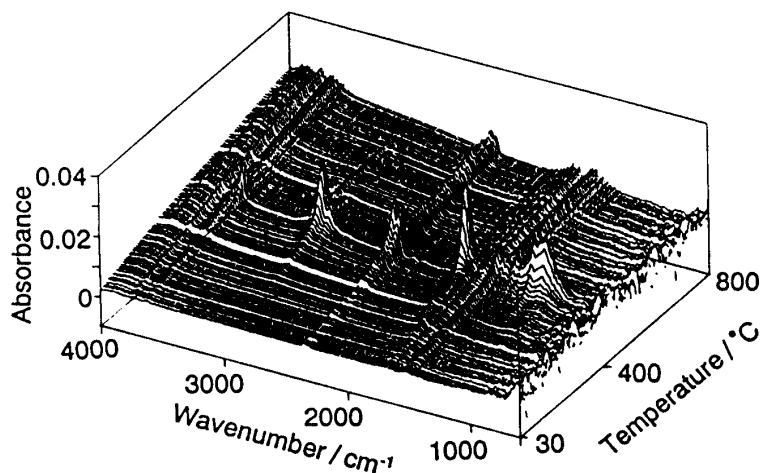


Fig. 5 Stacked IR spectra of epoxy resin with [AA/EPOXY] ratio 12/10.

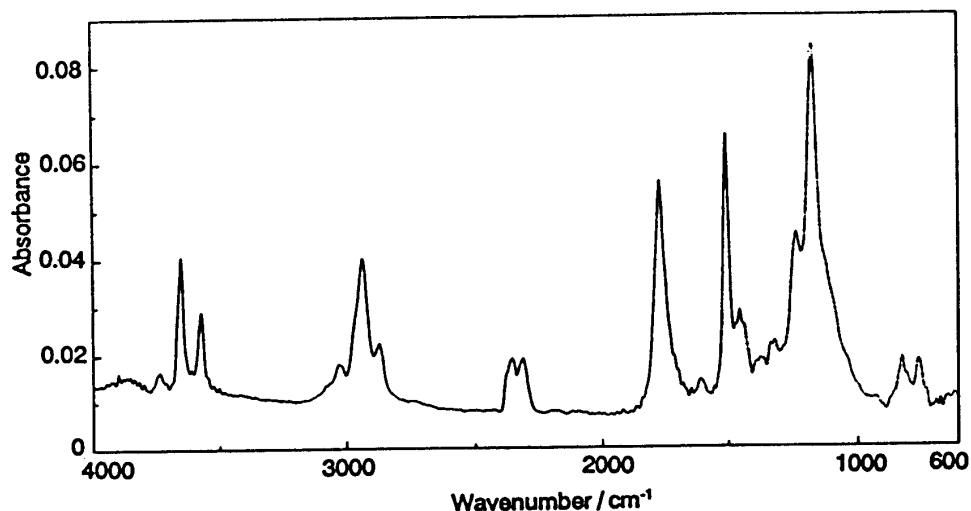


Fig. 6 IR spectrum of evolved gases during the thermal degradation of epoxy resin from HQ with [AA/EPOXY] ratio 12/10 at 400 °C.

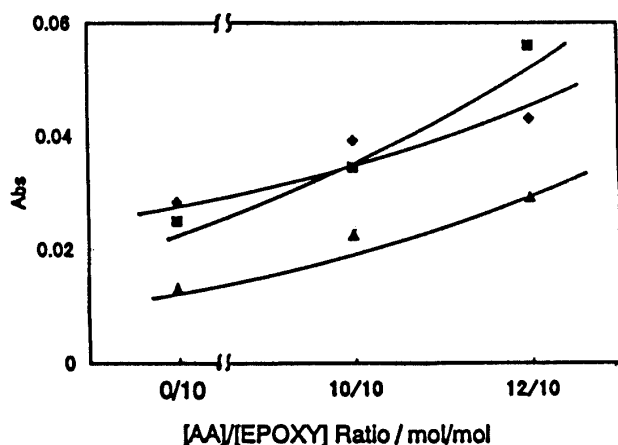


Fig. 7 Relationship between [AA]/[EPOXY] ratio and peak intensity at 2900 cm^{-1} (CH groups). (▲) AL, (■) HQ and (◆) MHQ.

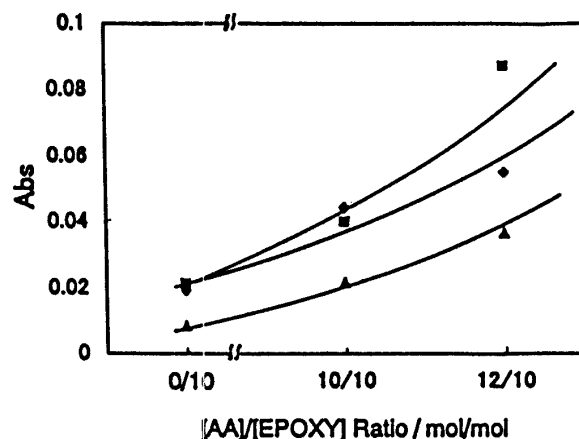


Fig. 8 Relationship between [AA]/[EPOXY] ratio and peak intensity at 1730 cm^{-1} (C=O groups). (▲) AL, (■) HQ and (◆) MHQ.

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