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Glass transition and thermal decomposition of epoxy resins from the carboxylic acid system consisting of ester-carboxylic acid derivatives of alcoholysis lignin and ethylene glycol with various dicarboxylic acids

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Abstract

Alcoholysis lignin (AL) was dissolved in ethylene glycol and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives of AL and ethylene glycol (AL-poly(ester-carboxylic acid), ALEGPA). The obtained ALEGPA was mixed with dicarboxylic acids with different alkylene chain length such as succinic acid (alkylene chain, C_2), adipic (C_4) acid and sebacic acid (C_8). The obtained mixture of ALEGPA and dicarboxylic acid was reacted with ethylene glycol diglycidyl ether in the presence of a catalytic amount of dimethylbenzylamine to form ester-epoxy resins. The curing reaction was carried out at 130 °C for 5 h. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios, mol/mol) was 1.0. The ALEGPA content in the above mixture was varied from 0 to 100%. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (T_g's) increased with increasing ALEGPA contents, suggesting that lignin acts as a hard segment in epoxy resin networks. The values of T_g's of epoxy resins with dicarboxylic acids increased in the following order; epoxy resins with succinic acid (alkylene chain, C_2), adipic acid (C_4) and sebacic acid (C_8). Thermal degradation temperatures (T_d's) of epoxy resins slightly decreased with increasing ALEGPA contents. The values of mass residue at 500 °C (MR_{500}) increased with increasing AL contents in epoxy resins and also with decreasing chain lengths of dicarboxylic acids.

Keywords: Glass transition; Thermal decomposition; Epoxy resins; Alcoholysis lignin; Aliphatic dicarboxylic acids

1. Introduction

Lignin is recognized as one of the most important renewable resources, since the amount of production is very large [1]. Lignin has a highly branched chemical structure consisting of phenyl propane units which are connected mainly by ether linkage. It is known that lignin shows insufficient mechanical properties in solid state as a polymeric material [2]. Many attempts in chemical and physical modifications of lignin have been made in order to solve the above problems in its utilization as a polymeric material. In the last 10 years, we have extensively studied synthetic polymers from lignin [3,4]. In the above studies, synthetic polymers were derived from lignin on the basis of molecular design concerning the basic structures such as phenyl propane units, and also the functional groups in lignin molecules such as hydroxyl and methoxyl groups. Recently, it was found that polyurethanes

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derived from lignin and also from lignin-based caprolactones show excellent thermal and mechanical properties and also biodegradability [5–9].

Epoxy resins are recognized as one of the important thermoset polymers, since they are used in various materials such as adhesives, matrix of composites and elastomers. In the past, many researchers studied ether type of lignin-based epoxy resins prepared from lignin [10–12]. Recently, aliphatic polyesters, such as polycaprolactones, poly ethylene succinate, polylactic acid, have received considerable attention due to the fact that they are biodegradable. 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 [13]. We also studied epoxy resins which can be prepared from an ester-carboxylic acid derivative of lignin synthesized from alcoholysis lignin (AL) and succinic acid anhydride. The obtained ester-carboxylic acid derivative of AL (ALEGPA) was reacted with ethylene glycol diglycidyl ether (EGDGE) to form epoxy resins under various conditions. The behavior in curing reactions was studied by differential scanning calorimetry (DSC). Furthermore, the thermal properties of the obtained epoxy resins were studied by DSC and thermogravimetry (TG) [14]. In the present study, epoxy resins were prepared from a carboxylic acid system consisting of ALEGPA with aliphatic dicarboxylic acids with different alkylene chain lengths such as succinic acid (alkylene chain, C_2), adipic acid (C_4) and sebacic acid (C_8). The thermal properties such as glass transition and thermal decomposition of the obtained epoxy resins were studied by DSC and TG. The influence of the difference in chemical structure of epoxy resins on thermal properties is investigated.

2. Experimental

2.1. Materials

Alcoholysis lignin (AL) was kindly supplied by Repap Co., USA, and was dried in vacuum at 70 °C. Other reagents such as ethylene glycol (EG), ethylene glycol diglycidyl ether (EGDGE), dimethylbenzylamine (DMBA), succinic acid, adipic acid and sebacic acid were commercially obtained from Wako Pure Chemical Industries Ltd., Japan. The above reagents were used without further purification.

2.2. Preparation of epoxy resins

AL polyacid (ALEGPA) was prepared from AL, EG and succinic anhydride, according to the method previously reported [14]. ALEGPA and a dicarboxylic acid (DCA) was mixed well with EGDGE at 80 °C, and the mixture was allowed to stand at 130 °C for 5 h in an oven. Each of succinic acid, adipic acid and sebacic acid was used as an aliphatic dicarboxylic acid (DCA). The molar ratios of carboxylic acid groups to epoxy groups [EPOXY]/[ACID] ratio ($\mathrm{mol\,mol^{-1}}$) was maintained at 1.0. ALEGPA contents were varied at 0, 20, 40, 60, 80 and 100%. The [EPOXY]/[ACID] ratios and the ALEGPA contents were calculated by the following equations:

$$[\mathrm{EPOXY}]/[\mathrm{ACID}]\ \text{ratio (mol/mol)} = (M_{\mathrm{EGDGE}} W_{\mathrm{EGDGE}})/(M_{\mathrm{ALEGPA}} W_{\mathrm{ALEGPA}} + M_{\mathrm{DCA}} W_{\mathrm{DCA}}),\ \text{ALEGPA content(\%)} = [W_{\mathrm{ALEGPA}}/(W_{\mathrm{ALEGPA}} + W_{\mathrm{DCA}})] \times 100$$

where M_{EGDGE} is the mole number of epoxy groups per gram of EGDGE (7.7 $\mathrm{mmol\,g^{-1}}$), W_{EGDGE} the weight of EGDGE, M_{ALEGPA} the mole number of carboxylic acid groups per gram of ALEGPA (6.62 $\mathrm{mmol\,g^{-1}}$), W_{ALEGPA} the weight of ALEGPA, M_{DCA} the mole number of carboxylic acid groups per gram of DCA, W_{DCA} the weight of DCA.

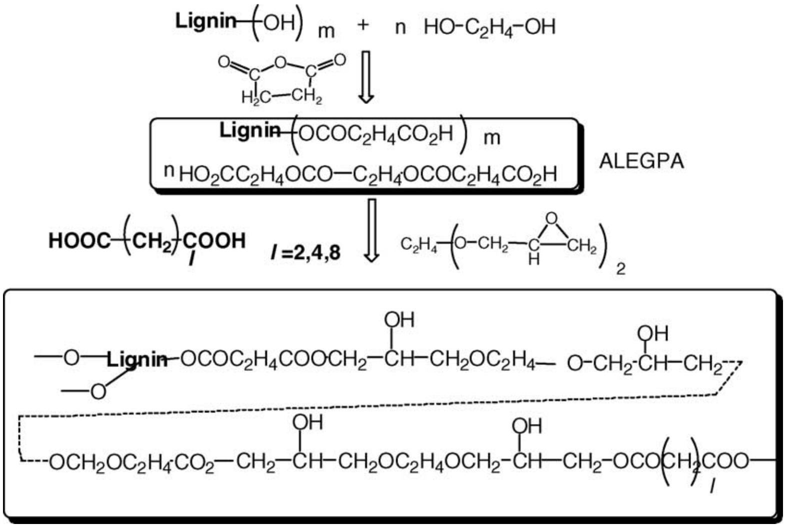
2.3. Measurements

A Perkin-Elmer Spectrum One Fourier transform infrared spectrometer equipped with a universal ATR unit was used for infrared spectrometry. A Seiko DSC 220 was used for differential scanning calorimetry (DSC). The measurements of glass transition of epoxy resins were carried out ranging from −60 to 80 °C at a heating rate of 10 $^\circ\mathrm{C\,min^{-1}}$ 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's) were determined according to a method reported by Nakamura et al. [15]. A Seiko TG/DTA 220 was used for thermogravimetry (TG). The measurements were carried out using ca. 5 mg of samples at a heating rate of 10 $^\circ\mathrm{C\,min^{-1}}$ in nitrogen flow of 300 $\mathrm{mL\,min^{-1}}$. Thermal decomposition temperatures (T_d's) were determined according to a method reported by Hatakeyama and coworkers [16].

3. Results and discussion

In the present study, epoxy resins were obtained by the reaction of a mixture ALEGPA/DCA with EGDGE. The reaction scheme is shown in Scheme 1. The chemical structure of the obtained ALEGPA is confirmed by FT-IR. FT-IR spectrum of ALEGPA is shown in Fig. 1. The characteristic absorption peaks of carboxylic acid groups at 1780, around 2700 and 3200 $\mathrm{cm^{-1}}$, and also of ester groups at 1720, 1200 $\mathrm{cm^{-1}}$ are observed in the spectrum. The FT-IR spectrum of an epoxy resin with succinic acid with ALEGPA content 60% after curing at 130 °C for 5 h is also shown in Fig. 1. The characteristic absorption peaks for ester groups 1720 and 1200 $\mathrm{cm^{-1}}$ and also hydroxyl groups at 3300 $\mathrm{cm^{-1}}$ are observed.

Glass transition of epoxy resins was studied by DSC. Fig. 2 shows DSC curves of epoxy resins with various ALEGPA contents. A heat capacity gap in baseline due to glass transi-



Scheme 1. Reaction scheme for the preparation of epoxy resins.

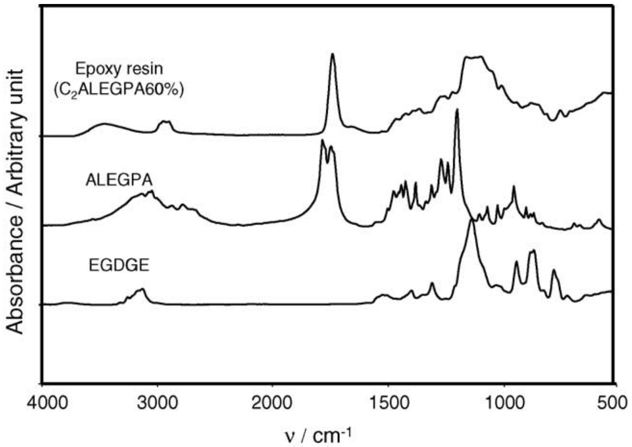


Fig. 1. FT-IR spectra of ALEGPA, EGDGE and an epoxy resin with succinic acid.

tion is observed in each DSC curve. T_g's change according to the change in ALEGPA contents of epoxy resins in the ALEGPA/succinic acid system. Fig. 3 shows the relationship between T_g and ALEGPA content of epoxy resins with dicarboxylic acids (DCA) with various alkylene chain lengths. T_g increases with increasing ALEGPA content of epoxy resin. The above results indicate that lignin acts as a hard segment in epoxy resin molecules. It is known that lignin is a highly branched polymer consisting of phenylpropane units mainly connected by ether linkage. It has also a number of hydroxyl groups in a molecule [1]. Therefore, it is considered that lignin exists as cross-linking points. The chain lengths of epoxy resins between cross-linking points decrease with increasing ALEGPA content in epoxy resins. The increase in the chain lengths between cross-linking points enhances the main chain molecular motion. The T_g values are high in the

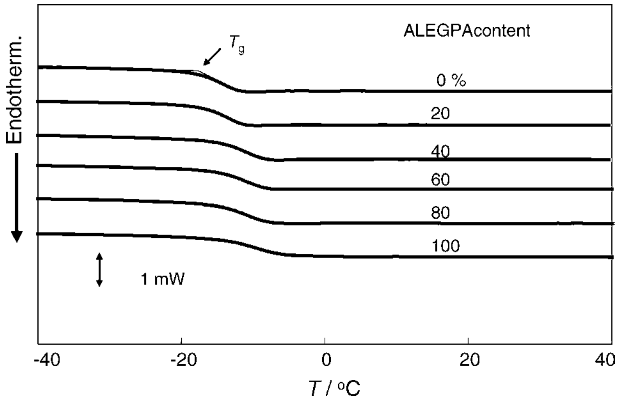


Fig. 2. DSC curves of epoxy resins with various ALEGPA contents in a ALEGPA/succinic acid system. Numbers indicate ALEGPA contents.

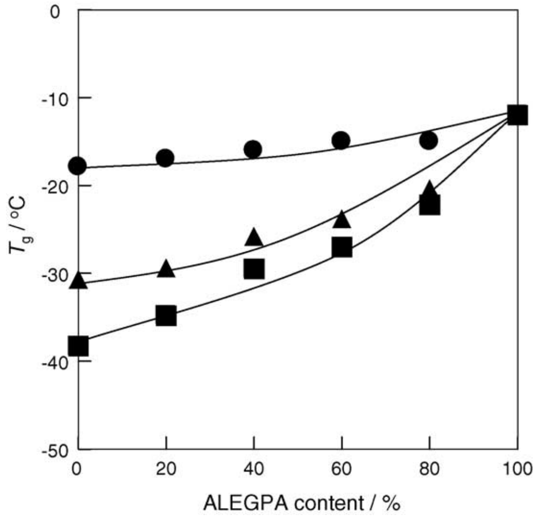


Fig. 3. Relationship between T_g and ALEGPA content of epoxy resins with DCA with various alkylene chain lengths. C_2 (●), C_4 (▲) and C_8 (■).

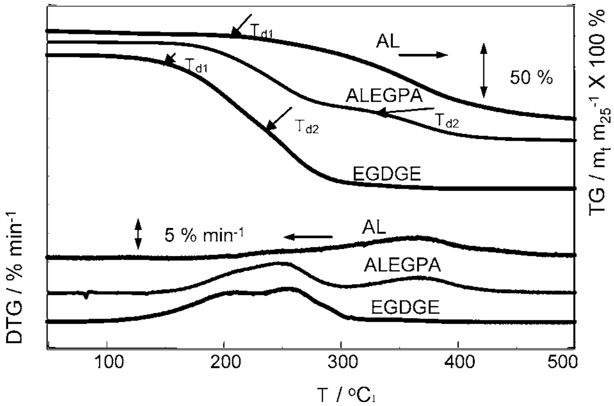


Fig. 4. TG and differential TG (DTG) curves of the starting materials such as ALPA, EGDGE and AL.

order of epoxy resins with succinic acid (C_2), adipic acid (C_4) and sebacic acid (C_8). The above results are reasonable when we consider that the flexibility of main chains in epoxy resin molecules increases with increasing chain lengths of dicarboxylic acids.

Thermal decomposition behavior of starting materials and epoxy resins was studied by TG. Fig. 4 shows TG and differential TG (DTG) curves of the starting materials such as ALEGPA, EGDGE and AL. TG and DTG curves of DCA are not shown in Fig. 4, since only the evaporation of the above compounds was observed in TG measurements. It is observed that thermal decomposition apparently proceeds in two steps. T_d's at lower temperature regions (T_{d1}) and also T_d's at higher temperature regions (T_{d2}) were determined. T_{d1}'s of the starting materials are 189.6 and 133.3 °C while T_{d2}'s 335.3 and 233.2 °C, respectively. It is known that epoxy groups are relatively unstable [17]. Accordingly, it is considered that the above group starts to decompose at T_{d1} region.

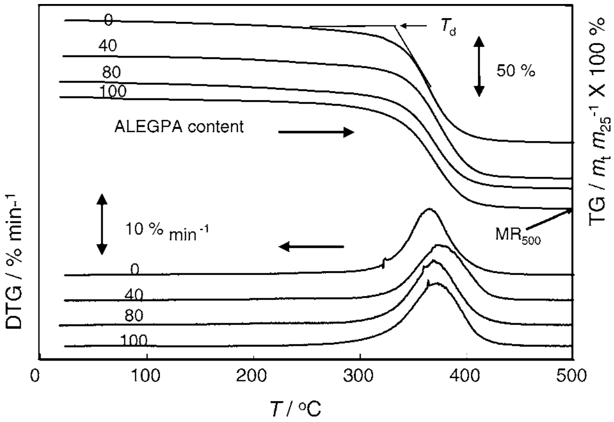


Fig. 5. TG and differential TG (DTG) curves of epoxy resins.

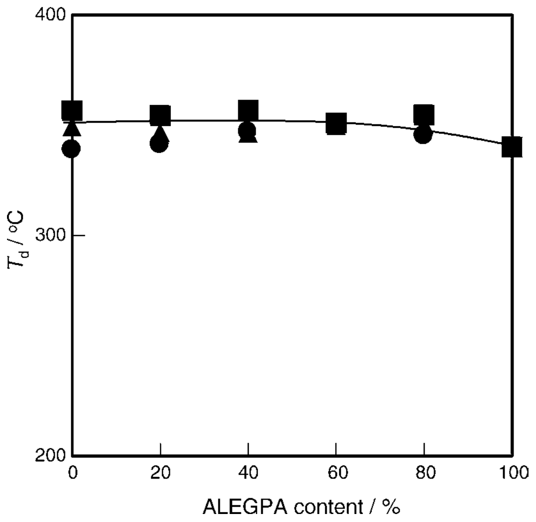


Fig. 6. Relationship between T_d ALEGPA content of epoxy resins. C_2 (●), C_4 (▲) and C_8 (■).

Fig. 5 shows TG and differential TG (DTG) curves of epoxy resins with various ALEGPA contents in the ALEGPA/DCA systems with succinic acid, adipic acid and sebacic acid. It is observed that the decomposition apparently proceeds in a smooth step. The thermal degradation at T_{d1} region, that is observed in TG curves of the starting materials (Fig. 4), is not observed. This indicates that thermally unstable carboxylic acid and epoxy groups were converted into thermally stable ester groups. Thermal decomposition temperatures (T_d's) and mass residue at 500 °C (MR_{500}) were determined from TG curves. Fig. 6 shows the relationship between T_d and ALEGPA content of epoxy resins. T_d slightly decreases with increasing ALEGPA content. However, the degree of the decrease in T_d values is very small. It is known that lignin is relatively thermally unstable [6]. As shown in Fig. 4, T_d of AL was determined as 284.3 °C. The T_d values of epoxy resins from AL are much higher than that of AL. Therefore, it can be considered that lignin becomes thermally stable after introduction into the epoxy resin molecules. As shown in Fig. 6, T_d values are almost the same regardless of the difference in alkylene chain lengths of DCA. In order to clarify the influence of lignin in epoxy resins on MR_{500} values, AL contents in epoxy resins were calculated. The relationship between AL contents and MR_{500} is shown in Fig. 7. As clearly seen in Fig. 7, MR_{500} values increase with increasing AL contents in epoxy resins. It is known that lignin molecules react with each other to form a condensed char-like material, when they are heated in nitrogen. Therefore, it is considered that the materials in the residue at 500 °C are mainly formed by the reaction with lignin in epoxy resins during the decomposition process. The above consideration can be supported by the fact that the MR_{500} value of ALEGPA is higher than that of SA, as shown in Fig. 4. As shown in Fig. 7, MR_{500} vales are always high in the order of epoxy resins with succinic acid (C_2), adipic acid (C_4) and sebacinic acid (C_8), suggesting that dicarboxylic acids with longer alkylene chains give smaller amounts of residual materials after thermal decomposition up to 500 °C. However, the above difference in MR_{500} values becomes smaller when AL contents are increased. Accordingly, it can be said that the AL contents in epoxy resins strongly affect MR_{500} values in the higher AL contents region.

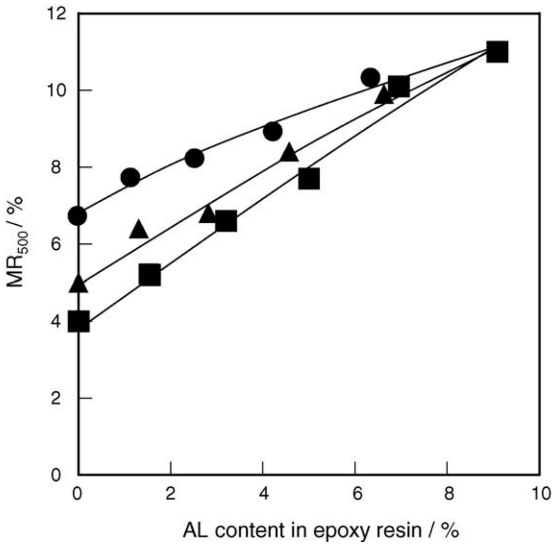


Fig. 7. Relationship between MR_{500}'s and AL contents in epoxy resins. C_2 (●), C_4 (▲) and C_8 (■).

4. Conclusion

Epoxy resins were obtained by the reaction of the ester-carboxylic acid derivatives of alcoholysis lignin (ALEGPA)/aliphatic dicarboxylic acids (DCA) system with EGDGE. T_g increased with increasing ALEGPA contents in epoxy resins, suggesting that lignin acts as a hard segment in epoxy resins. It was found that T_g's of epoxy resins decreased with increasing alkylene chain lengths of dicarboxylic acids from C_2 to C_8. T_d slightly decreased with increasing ALEGPA content in epoxy resin. The difference in alkylene chain length of DCA does not affect T_d values of epoxy resins, while it affects MR_{500} values. It was also found that AL contents in epoxy resins strongly affect MR_{500} values particularly in the higher AL contents region.

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