Journal of Oil Palm Research Vol. 23 August 2011 p. 1110-1114

NEW EPOXY RESINS FROM OIL PALM COMPONENTS

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ABSTRACT

New types of epoxy resins, which are derived from plant components, such as saccharides and lignin, have been developed in our laboratory. Oil palm components such as lignin, saccharides, lignocellulose, glycerol and fatty acids can be included in the above epoxy resin system. Alcoholysis lignin (AL) was dissolved in glycerol (GLY) and ethylene glycol (EG), and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-GLY polyacid, ALGLYPA and AL-EG polyacid, ALEGPA). The mixture of ALEGPA and ALEGPA was allowed to react with glycerol diglycidyl ether (GLYGDE) in the presence of a catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups (EPOXY/ACID ratio, mol mol^{-1}) was maintained at 1.0. The contents of ALGLYPA in the mixture of ALGLYPA and ALEGPA (ALGLYPA content) were varied from 0% to 100%. The thermal properties of the epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperature (T_g) of the epoxy resins increased with increasing ALGLYPA content, suggesting that the lignin and glycerol structures act as hard segments in the epoxy resin networks. Thermal decomposition temperature (T_d) of the epoxy resins was almost constant regardless of ALGLYPA content.

Keywords: epoxy resins, lignin, glycerol, oil palm.

Date received: 8 May 2010; **Sent for revision:** 2 September 2010; **Received in final form:** 25 April 2011; **Accepted:** 12 July 2011.

INTRODUCTION

The main plant components such as cellulose, hemicellulose and lignin are recognised as important renewable resources, because the amount of their production is large (Kringstad, 1980). Mono- and disaccharides such as glucose, fructose and sucrose are also abundantly produced from sugar-cane and other plants (Lichtenthaler and Mondel, 1997). Therefore, the possible utilisation of the above plant 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 (Kennedy *et al.*, 2001). In the last 10 years, synthetic polymers derived from saccharides and lignin, which are the main components of plant materials, have been extensively studied by our research group (Hatakeyama *et al.*, 1995; Hatakeyama, 2002). The above studies have been carried out on the basis of the molecular design concerning the functional groups in their molecules such as pyranose and furanose rings, as well as phenylene, hydroxyl and methoxyl groups. Recently, it was found that polyurethanes derived from lignin, molasses, mono- and disaccharides and also from saccharide-based caprolactones show excellent thermal and mechanical properties, and also biodegradability (Hatakeyama *et al.*, 2003; Hatakeyama and Hatakeyama, 2004; Hatakeyama and Hatakeyama, 2005).

Epoxy resins are known to be one of the important thermoset polymers, because they are used as various materials, such as adhesives, composite matrices and elastomers (Bhatnagar, 1996). Aliphatic polyesters, such as polycaprolactones, poly(ethylene succinate) and poly(lactic acid), have received considerable attention due to the fact that

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they are biodegradable (Albertsson and Varma, 2002). In our previous study, we investigated the synthesis and thermal properties of the ester type of epoxy resins, which can be derived from lignin, polyethylene glycol diglycidyl ether and azelaic anhydride (Hirose *et al.*, 2001). Epoxy resins were also prepared from an ester-carboxylic acid derivative of lignin such as alcoholysis lignin (AL) and sodium lignosulfonate, and from saccharides such as glucose, fructose and sucrose (Hirose *et al.*, 2003a, b; 2005a, b; Maznee *et al.*, 2010). Various plant components can be included into epoxy resin networks. Oil palm-based biomass includes palm oil and lignocellulosics such as trunks, fronds and empty fruit bunches (Sun *et al.*, 1999a, b; Wan Rosli *et al.*, 2007). In the present study, as an example of utilisation of oil palm components, ester-carboxylic acid derivatives were synthesised from AL and glycerol (GLY). The obtained ester-carboxylic acid derivative of AL was allowed to react with glycidyl compounds from vegetable oil components such as glycerol diglycidyl ether (GLYDGE) to obtain epoxy resins under various conditions. The thermal properties of the obtained epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

EXPERIMENTAL

Materials

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

Synthesis of Ester-carboxylic Acid Derivatives of AL, GLY and EG

AL polyacid (ALGLYPA) was obtained as follows: AL was dissolved in GLY at 80°C. Succinic anhydride and a catalytic amount of DMBA were added to the above solution, and the mixture was stirred at 80°C for 6 hr. ALEG polyacid (ALEGPA) was also prepared from AL and EG in the same manner as ALGLYPA. The synthesis scheme of the process is shown in *Figure 1*.

Synthesis of Epoxy Resins

ALGLYPA was mixed well with GLYDGE at 80°C, and the mixture was allowed to stand at 130°C for 5 hr in an oven. The synthesis scheme of the epoxy resins is shown in *Figure 2*. The molar ratio of the carboxylic acid groups to the epoxy groups [EPOXY/ACID ratio (mol mol^{-1})] was maintained at 1.0. The ALGLY contents were also varied at 0%, 20%, 40%, 60%, 80% and 100%. The ALGLYPA

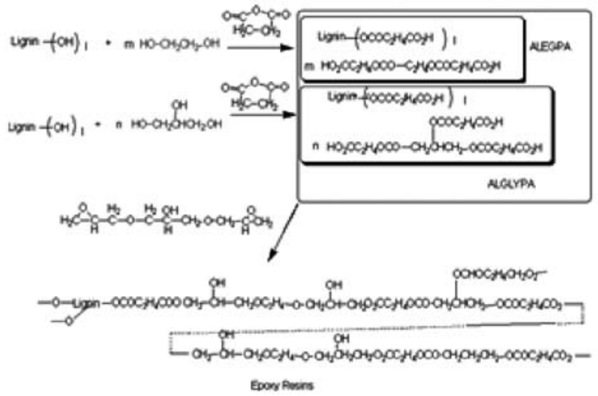

Figure 2. Reaction scheme for synthesis of epoxy resins from ALEGPA, ALGLYPA and GLYDGE.

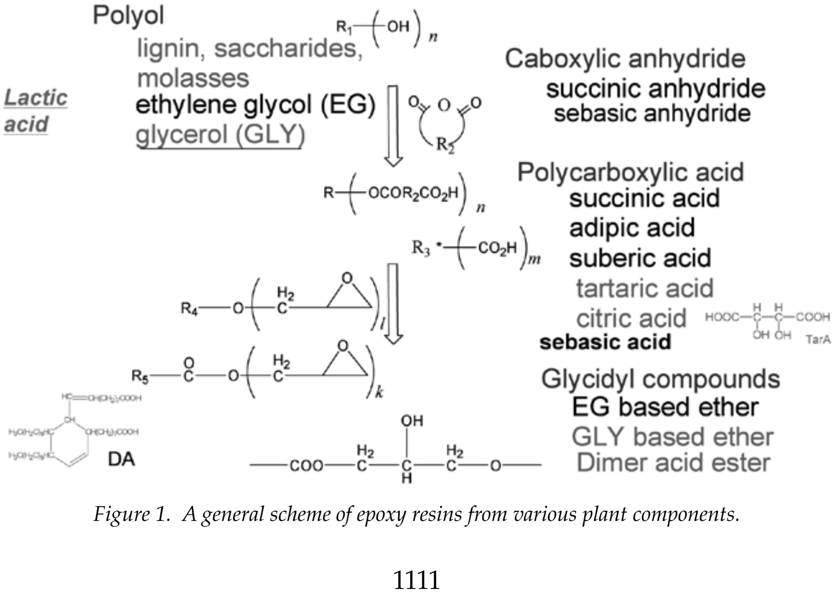

Figure 1. A general scheme of epoxy resins from various plant components.

contents by weight (W) were calculated by the following equation:

$$\text{ALGLYPA content (\%)} = \left[\frac{[W_{ALGLYPA}}{(W_{ALGLYPA} + W_{ALEGPA})}\right] \times 100$$

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 DSC. The measurements of phase transition of the epoxy resins were carried out ranging from -60°C to 80°C at a heating rate of 10°C min^{-1} using ca. 5 mg of sample. The samples were heated to 130°C and maintained for 10 min, and then quenched to -60°C in DSC aluminum vessels before the measurements were made. The glass transition temperatures (T_g's) were determined according to the method reported by Nakamura *et al.* (1988). The heat capacity gap at T_g (ΔC_p) was also determined using the DSC curves. A Seiko TG/DTA 220 was used for TG. The measurements were carried out using ca. 5 mg of sample at a heating rate of 10°C min^{-1} in a nitrogen flow of 300 ml min^{-1}. Thermal decomposition temperatures (T_d's) were determined according to the method reported by Hatakeyama and Quinn (1994). Mass residues at 500°C (MR_{500}'s) were also determined for each of the samples.

RESULTS AND DISCUSSION

Epoxy resins were obtained by the reaction of ALGLYPA and ALEGPA with GLYDGE. The reaction scheme is shown in *Figure 2*. The chemical structure of the obtained epoxy resins was analysed by FTIR. The FTIR spectra of ALGLYPA and ALEGPA are shown in *Figure 3.* The characteristic absorption peaks of the carboxylic acid groups at ca. 1690, around 2650 and 3000 cm^{-1}, and also of the ester groups at 1730 and 1200 cm^{-1} can be observed in the spectra. The FTIR spectrum of an epoxy resin from ALGLYPA and GLYDGE after curing at 130°C for 5 hr is also shown in *Figure 3*. The characteristic absorption peaks for the ester groups at 1730 and 1200 cm^{-1} and also the hydroxyl groups at 3450 cm^{-1} can be observed, while the characteristic peaks of the carboxylic acid groups at 1690, 2650 and 3000 cm^{-1} are not apparent. The results suggest that the carboxylic acid groups had been converted into the ester groups with hydroxyl groups at β-carbon after the curing reaction.

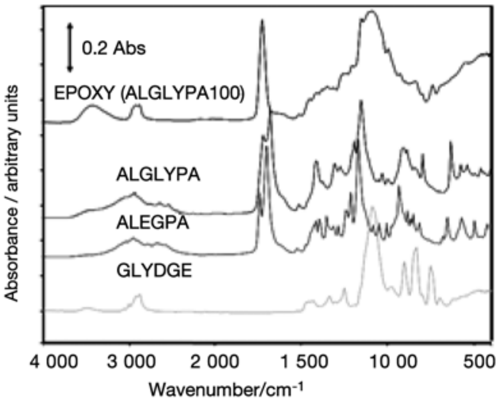

Figure 3. FTIR spectra of ALGLYPA, ALEGPA, GLYDGE and epoxy resin.

Phase transition of the epoxy resins was studied by DSC. *Figure 4* shows the DSC curves of the epoxy resins with various ALGLYPA content. The T_g change according to the change in ALGLYPA content of the epoxy resins. *Figure 5* shows the changes in T_g and ΔC_p against ALGLYPA content of the epoxy resins. The T_g increase with increasing ALEGPA content, while ΔC_p decreases with increasing ALGLYPA content of the epoxy resin, although the ΔCp data are somewhat scattered. These results indicate that lignin and glycerol act as the hard segments in the epoxy resin molecules. Accordingly, it is suggested that lignin and glycerol exist as cross-linking points, and that the chain lengths of the epoxy resins

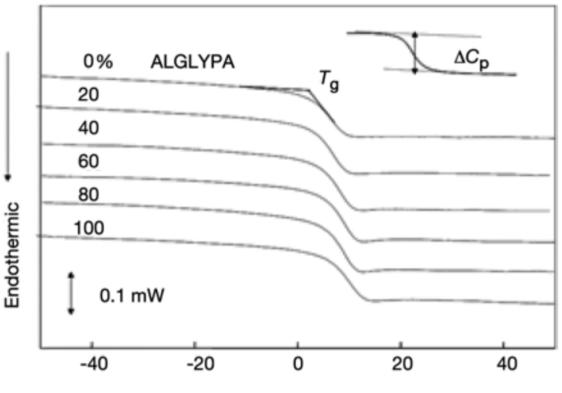

Figure 4. DSC curves of epoxy resins at varying ALGLYPA content.

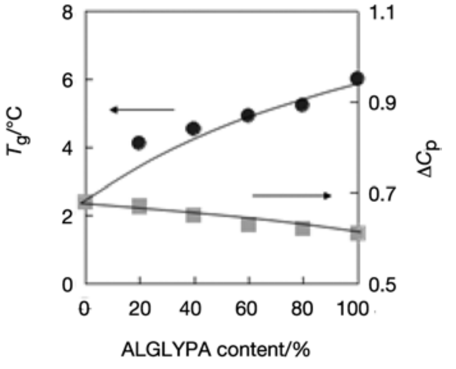

Figure 5. Changes in T_g and ΔC_p against ALGLYPA content.

between the cross-linking points decrease with increasing ALGLYPA content in the epoxy resins. The increase in the chain lengths between the cross-linking points enhance the main chain molecular motion.

The thermal decomposition behaviour of the starting materials and the epoxy resins was studied by TG. *Figure 6* shows the TG and DTG curves of the epoxy resins at varying ALGLYPA content. It is observed that the decomposition apparently proceeds in a smooth step, without thermal decomposition at the lower T_d region, which was apparent in the TG curves of the starting materials. This indicates that the thermally unstable carboxylic acid and epoxy groups were converted into thermally stable ester groups. Thermal decomposition temperatures (T_d's) and mass residues at 500°C (MR_{500}'s) were determined from the TG curves. *Figure 7* shows the relationship between T_d and ALGLYPA content of the epoxy resins. The T_d is almost constant regardless of ALGLYPA content. It has been reported that lignin is relatively thermally unstable (Hirose *et al.*, 1998). Therefore, it can be thought that lignin becomes thermally stable after introduction into the epoxy resin molecules. *Figure 7* also shows the relationship between MR_{500} and ALGLYPA content of the epoxy resins. The MR_{500} value is almost constant regardless of ALEGPA content. It is known that lignin molecules react with each other to form a condensed char-like material when it is heated in nitrogen. Therefore, it is suggested that the materials in the residue at 500°C are mainly formed by reaction with lignin in the epoxy resins during the decomposition process.

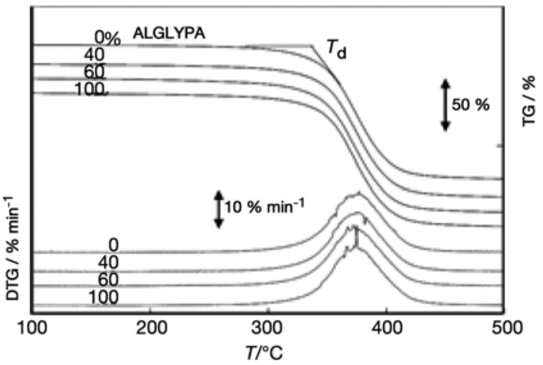

Figure 6. TG and DTG curves of epoxy resins at varying ALGLYPA content.

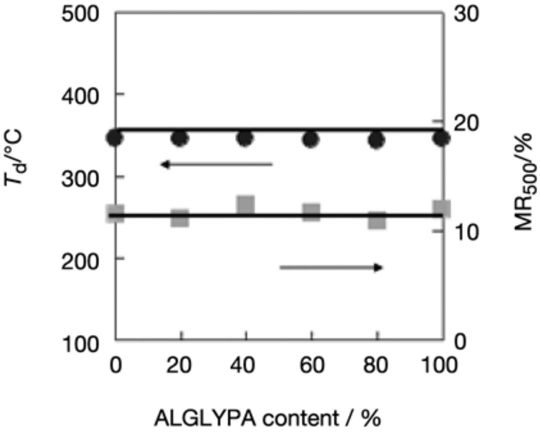

Figure 7. Changes of T_d and MP_{500} against ALGLYPA content.

CONCLUSION

The obtained results suggest that oil palm components such as lignin and glycerol can be introduced into the new epoxy resin system. Palm oil components such as glycerol and fatty acids have potential to be used as epoxy resin components such as polyols and epoxy compounds, *i.e.* glycerol-based epoxy compounds and dimer acid-based epoxy compounds. Oil palm biomass such as trunks, fronds and empty fruit bunches are known to be lignocellulosics (Sun *et al.*, 1999a, b; Wan Rosli *et al.*, 2007). Saccharides, ethanol, lactic acid and other chemicals are produced from cellulose and hemicellulose, and lignin can be obtained as a by-product in the above processes. Fibrous materials can also be obtained from oil palm biomass. These materials can be used as fillers in various composite materials.

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