AN INVESTIGATION OF PHYSICAL PROPERTIES OF AN EPOXY RESIN FOR SINGLE COMPONENTS

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Abstract

Deriving chemicals from renewable feedstock has become a necessity to reduce dependency on petroleum, which release carbon dioxide when burned and aggravate the global warming and ocean acidification. This work offers a potential alternative - bark extractives based epoxy resin - to petro-based conventional epoxy. Our results showed successful epoxidation of bark extractives after reaction with epichlorohydrin. The newly synthesized epoxy (E-epoxy) can replace 50% of petroleum-based epoxy (P-epoxy) and the blend system displayed thermal stability and tensile strength comparable to neat P-epoxy, which demonstrates a great promise in using bark extractives as a substitute for BPA. An examination of reaction parameters showed that the E-epoxy monomer can be synthesized with high yield and reactivity using spray-dried extractives as substrates, a dioxane/water combination as solvent, and tetrabutylammonium hydroxide as the ring-opening catalyst. An examination of numerical parameters showed the maximum yield with minimum epoxy equivalent weight was achieved after 4.5 hours reaction time with sodium hydroxide to hydroxyl value molar ratio of 3.4 at a reaction temperature of 80 °C. The thermal properties of E-epoxy were studied using TGA, FTIR, and Py-GC/MS, and a new thermal degradation mechanism was proposed.

Introduction

Epoxy resins are a class of high-performance thermosetting precursors, containing oxirane groups that can be cured by a diversity of co-agents, such as amines and anhydrides, to form three-dimensional networks. The cured epoxy resins, also called epoxies, hold a dominant position in the polymer market - especially in the automotive, construction, electronic and aerospace industries - due to their high strength, superior chemical-resistance, good compatibility with other materials, and minimum shrinkage and volatility of by-products after curing. The global demand of epoxy resin was estimated at roughly US$18.6 billion in 2013 and was forecasted to reach US$25.8 billion by 2018[1]. This increase in value reflects the increasing demand of epoxy resins in the global market over the coming years.

Additionally, the major component of epoxy resins, bisphenol A (BPA), is considered a toxic substance, and is included in Schedule 1 of the Canadian Environmental Protection Act[2] for declaring the necessity to substitute BPA. In conjunction with the scarcity of crude oil, replacing BPA with natural resources is evident, and thus many natural resources have been explored to determine their feasibilities as alternatives. Vegetable oil[3-5], liquefied wood[6-7] and lignin[8-9] are considered as the most promising materials with which to synthesize bio-based epoxy resins. Although epoxidized vegetable oils are already commercialized and commonly used as plasticizers, the structure of vegetable oil, containing only aliphatic chains, limits its mechanical strength and thermal stability[10]. Moreover, liquefied biomass contains more aromatic structures compared to epoxidized oil, but the liquefaction process is energy-intensive and uses toxic solvents like phenol[11]. Furthermore, lignin, a by-product of the paper industry, has abundant aromatic structures, but its viscosity and the molecular weight create difficulties during the manufacturing process. Therefore, finding a suitable natural resource to produce bio-epoxy resins remains one of the most important areas of interest.

The overall objective of this study is to better

understand the performance of extractive-based epoxy resin (E-epoxy), and its feasibilities to replace petroleum-based epoxy resins (P-epoxy). Each chapter of this present study was designed to reach the following sub-objectives:

1. Examining the feasibility of epoxidation reaction between bark extractives and ECH, which leads to the development of an innovative bio-epoxy;
2. Studying the effect of synthesis conditions on the yield, reactivity and molecular structures of E-epoxy;
3. Understanding the thermal stability and degradation kinetics of E-epoxy compared with other types of epoxy resins;
4. Investigating the influence of NCFs on the curing behaviour of P-epoxy; and
5. Assessing the effect of NCFs on mechanical strength of E-epoxy/P-epoxy blended system.
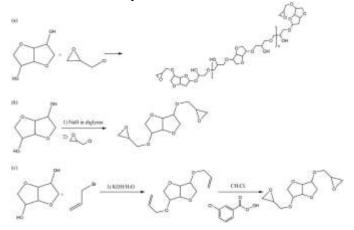
Saccharide-based Epoxy Resins

Carbohydrates are also a renewable resource with potential to be used as a petroleum-based polymers alternative. Some sugar-based building blocks have been studied intensively, such as monosaccharide (sorbitol), disaccharides (sucrose and isosorbide) and derived acid compounds (lactic acid, succinic acid, itaconic acid, and levulinic acid). However, the hydroxyls on saccharide compounds have high pKa values compared to phenolic hydroxyls, which means the reactivity of alcohol groups toward ECH is lower than that of phenol groups. These alcohol groups have to compete with the new generated hydroxyls from the reactions with ECH, which results in incomplete dehydrochlorination reactions. Thus, saccharide-based epoxy resins require a different technique to synthesize high quality products.
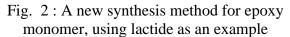
Sorbitol is a hydrogenized alcohol sugar of glucose and has been selected as one of the top 12 potential bio-based platform chemicals by the U.S Department of Energy24. Sorbitol polyglycidyl ether has been produced as well-established commercial products such as DENACOL™ and ERISYSTM. However, due to the incompleteness of the dehydrochlorination
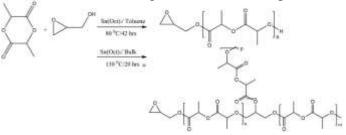
reaction, these commercial products contain about 10−20 wt % chlorine, which embrittles the epoxy network, and undergoes HCl formation1. Furthermore, compared to DGEBA, its Tg and mechanical performance remain low25.

However, the thermal stability of epoxidized isosorbide can be an issue, as it contains large amount of oxygen in its ring structures and two hydroxyl groups in each repeat unit. Based on the thumb rule of structure-stability relationship, these oxgen-containing groups are weak links which can significantly reduce the thermal stability of epoxidized isosorbide.

Fig. 1 Synthesis of diglycidyl ether of isosorbide by various methods

Fig. 2 : A new synthesis method for epoxy monomer, using lactide as an example

Sugar-based acids are high-potential candidates for green chemistry, and their acid groups have a strong tendency to react with ECH groups. Surprisingly, few research studies have focused Synthesis of Bark Extractive Epoxy Resins.

E-epoxy was prepared following a similar method to that reported for commercially available resins. Bark extractives (15 g), epichlorohydrin (150 g), solvent (1,4-dioxane, 150 g) and phase transfer catalyst (tetrabutylammonium hydroxide solution, 2 mL) were placed in a round bottom 3-neck glass flask and the temperature was raised to 60 °C while

stirring. An excess of epichlorohydrin was used in a mass ratio of bark extractives to epichlorohydrin of 1 to 10. The experiments were carried out following a two-factor design, including three synthesis temperatures (40 °C, 60 °C, 100 °C) and three sodium hydroxide amounts (0.5 mol, 1 mol, 2 mol). 50% w/w sodium hydroxide(aq) was then slowly added to the mixture using a pressure-equalizing dropping funnel while stirring. The flask was kept at 60 °C for a total of 6 hours to achieve the addition reaction of epichlorohydrin and the ring formation of epoxy groups. The products were then diluted and washed with acetone, and the solution was filtered to remove salt. The acetone and non-reacted epichlorohydrin in the filtered resin solution were evaporated using a rotary evaporator at 120 °C under reduced pressure. Lignin-based epoxy resins and cellulose-based epoxy resins were prepared following the same extraction and synthesis procedure as that described. The replicate of each sample is one.

To understand better the influence by the major components in the bark extractives, the IR spectra of epoxidized lignin extractives (L-epoxy) and epoxidized cellulose extractives (C-epoxy) are shown in Fig. 3-2 (b). L-epoxy showed strong aromatic stretch absorption bands at 3052 cm-1 (C-H stretch), 2263 cm-1 / 2033 cm-1 (Ring substitution pattern), and 1632 cm-1 /1501 cm-1 (Ring stretch). In contrast, C-epoxy had a long-chain band absorption at 710 cm-1 and a strong alcohol vibration at 1113 cm-1 which also appeared on the E-epoxy IR spectrum.

Fig: 3 FTIR spectra of (a) bark extractives, epoxidized bark extractives and commercial epoxy resin, (b) bio-epoxy resins

Origin software (version 8.6; Microcal Software Inc., Northampton, MA) was used to separate the multi-peaks in the GPC results. Three peaks were identified in E-epoxy and four peaks were identified in L-epoxy. Comparing Fig. 3-7 (a) with (b), the first peak of L-epoxy is 3891 Da, which is similar to the molecular weight reported for alkali lignin by other researchers26, 35. We suggest that the first peak of E-epoxy (1071 Da) and the second peak of L-epoxy (1396 Da) are from epoxidized lignin fragments with 5 or 6 monolignol monomers. The second peak of E-epoxy (513 Da) may be an epoxidized catechin which reacted with four epichlorohydrin units. This is a likely explanation since the peak of 528-529 Da is the most common repeating unit shown in commercial tannins31. The third peak (345 Da/372 Da) and fourth peak (277 Da) might be assigned to the epoxidized resin acid and epoxidized coniferyl alcohol, respectively.

Table 1 : Molecular weight and polydispersity of E-epoxy and L-epoxy

	Mn	Mw	PDI	Peak1	Peak2	Peak3	Peak4
E-epoxy	588 (26)	796(21)	1.36	1071	513	345	-
L-epoxy	1071(43)	2210(39)	2.06	3891	1396	372	277

Individual molecular bonds and bond groupings vibrate at characteristic frequencies and selectively absorb infrared radiation at matching frequencies. Thus, the amount of radiation absorbed or passed through unchanged is dependent on the sample's chemical composition; the resultant curve is known as an infrared spectrum. The uniqueness of the molecule's infrared spectrum is derived from the combination of certain atomic groupings within that molecule. These particular give rise to characteristic absorptions which can be independent of the rest of the molecule and/or affected by location of neighboring groupings. They include all of the common organic functional groups (C=0, C=C, C-H, CH3, etc.) as well as many inorganic ones (-O-H, -N-H, SO2, etc.). Tables of characteristic

infrared group frequencies are helpful for identifying unknown materials from their spectra.

Fusion Temperature: - At this temperature unreacted epoxy resin react.

Fusion temperature is that temperature at which the cured sample started melting or fusing at this temperature the cured resin comes in fused for this purpose used Gel time apparatus and the temperature increased uniformed at the sample is noted carefully the state comes when the tip of sample start fusing which is the fusion temperature of sample is determination fusing temperature of samples one to resin is shown in the table given below.

Apparatus used: - Thermometer, Gel time appartus etc.

Observations: -

(i) Fusion temperature of single component epoxy resin effect to the Accelerator.

Changing Concentration of Accelerator keeping the concentration of hardener

Samples	Concentration of Accelerator	Concentration of hardener	Fusion temperature
Sample No. 1	1 gm	15 gm	129^0 C
Sample No. 2	1.25 gm	15 gm	113^0 C
Sample No. 3	1.30 gm	15 gm	106^0 C

(ii) Fusion temperature of single component epoxy resin effected by hardener (D.C.D.A)

Changing the Concentration of hardener and keeping the concentration of accelerator

Samples	Concentration of Accelerator	Concentration of hardener	Fusion temperature
Sample No. 1	1 gm	18 gm	58^0 C
Sample No. 2	1 gm	12 gm	102^0 C
Sample No. 3	1 gm	9 gm	146^0 C

Result: -

Concentration of Accelerator increase then fusion temperature of single component epoxy resin decrease as shown in graph.

Concentration of hardener (D.C.D.A) decrease then fusion temperature of single component epoxy resin in increase as shown in graph.

DIFFERENTIAL SCANNING CALORIMETRY: - TO EVALUATE GLASS TRANSITION TEMPERATURE.

Differential scanning calorimetry (DSC) is designed to measure the amount of energy absorbed (endotherm) or given off (exotherm) by a material as a function of temperature. Temperature differences between a sample and an inert reference material are recorded as a function of the sample temperature with the area under the output curve being directly proportional to the total energy (q) transferred into or out of the sample. The ordinate of the resultant thermogram, therefore, is proportional to the rate of heat transfer (dq/dt) at any given time. Because of its sensitivity to any reaction involving heat flow changes, DSC is especially useful for studying the sure of reactive epoxy systems. A combination of dynamic and isothermal experiments and provide information on reaction rates, cure rates, specific heat, and degree of cure. A typical dynamic DSC curves for an epoxy-based material. Identifiable critical points on the curve are shown.

The type and number of competing chemical reactions, heat of reaction, thermal conductivity, and specific heat of material at various stages of reaction produce temperature variations during a cure cycle that directly affect the final degree of

cure.

Control of resin advancement in raw material as well as degree of cure following processing is essential in order to ensure the quality and reliability of the final product. Because the curing of epoxy thermosets is accompanied by the liberation of heat, it follows that DSC is an excellent tool for these determinations. Indeed, DSC has been used for QC and degree of cure studies epoxy molding compounds, epoxy - glass printed circuit board prepregs, epoxy powder coatings an ambiently cured field repair epoxy system, graphite - epoxy prepreg resin matrices and film adhesives.

The degree of cure (Dc) or fraction reacted (●) can be determined from the total heat of reaction, ●HT, of the curing reaction and the residual heat of reaction, •Hresid, of the partially polymerized material. Dc can be calculated from dynamic DSC experiments as follows:

Dc=(●HT-•Hresid X 100)/(●HT)

To obtain fraction reacted versus time plots at various temperatures, which are very useful for cure cycle and processing studies,

Conclusion

The thermal behaviour and degradation compounds of E-epoxy monomer and its cured network. TGA, FTIR, and Py-GC/MS provide some insight into its lower thermal performance in comparison with that of P-epoxy resin. For uncured E-epoxy monomer, DTGA data shows a similar pattern to alkali lignin and abietic acid. Py-GC/MS detected significant amounts of dehydroabietic acid and lignin fractions at relatively low degradation temperatures (70-350 °C). Moreover, other extractive compounds from bark skeletal structures during the degradation at these temperatures were identified as cycloheptatriene, and diterpene. Based on the FTIR results, dehydration reactions occurred when bio-epoxy monomer was heated up to 200 °C. There were also some carboxylic compounds at high degradation temperatures (300-400 °C). On the other hand, cured E-epoxy resin shows two distinct degradation peaks in the DTGA

analysis, with one of the peaks appearing at 392 °C, which represents the degradation of HCN bonds. Furthermore, Py-GC/MS provided more detailed analysis of the cured E-epoxy resin compositions, such as diethyl phathalic, epimanool, methoxy-vinyl phenol, and stearic acid. Therefore, the substandard thermal performance of E-epoxy resin can be explained by the presence of these monofunctionalized diterpene and fatty acid molecules.

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