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Synthesis of biobased epoxy and curing agents using rosin and the study of cure reactions

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Rosin is an abundantly available natural product. Rosin is a mixture of acidic (*ca*. 90%) and neutral (*ca*. 10%) compounds. The characteristic fused ring structure of rosin acids is analogous to that of some aromatic compounds in rigidity, and makes rosin and its derivatives potential substitutes for those aromatic compounds in polymers. In this study, the synthesis of biobased epoxy and curing agent using rosin and the cure reaction were investigated. Abietyl glycidyl ether and methyl maleopimarate were synthesized from one of the rosin acids. Abietyl glycidyl ether was used as a model compound representing rosin-based epoxies, while methyl maleopimarate was used as a model compound representing rosin-based anhydride curing agents. The synthesis methods of the model compounds were examined and the chemical structures were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR and ESI-MS. Curing of abietyl glycidyl ether with aniline and curing of methyl maleopimarate with phenyl glycidyl ether were investigated separately. Nonisothermal curing of the model systems was studied by DSC, and the cured products were characterized by ^{1}H NMR.

Introduction

Rosin is an abundantly available natural product. Rosin is mainly obtained from the exudation of pines and conifers. It is also obtained by the distillation of crude tall oil, which is a byproduct in the Kraft pulp process, or from aged pine stumps. Total world production of rosin is approximately 1.2 million tons annually.[1] Rosin is a mixture of acidic (*ca*. 90%) and neutral (*ca*. 10%) compounds.[2] The acidic components, generally named rosin (or resin) acids, are also a mixture containing mainly isomeric abietic-type acids (40–60%) and pimaric-type (9–27%) acids on the basis of total rosin weight.[1] The exact composition of rosin acids varies, depending on the tree species and production location. Rosin and its derivatives have long been used as adhesive tackifiers, and are still mainly used in that market. In addition, rosin and its derivatives have also found other niche applications in printing, varnishes, paints, sealing wax, some soaps, paper sizing, soldering, plasters, *etc.*[2]

In recent years, the drive for obtaining chemicals and materials from renewable resources has also prompted the research of new applications for rosin. Rosin acids, owing to their characteristic fused ring structure, are analogous to many aromatic compounds in rigidity. Therefore, rosin and its derivatives could become important alternatives to current fossil carbon-based aromatic monomer compounds in polymers. The chemical reactivity of rosin resides in its monocarboxylic acid and the unsaturated carbon–carbon double bonds. The Diels–Alder adduct of levopimaric acid (one of the isomeric rosin acids) and maleic anhydride, the maleopimaric acid, for example, was used for polyesterimide[3] and polyamideimide.[4,5] Rosin-based polyols were also prepared and applied to polyurethane synthesis.[6–8] The adduct of levopimaric acid and acrylic acid was used to synthesize polyesters and polyamides.[9] Maleopimaric acid was also used as a rigid building block in aliphatic copolyesters to regulate molecular rigidity.[10,11] On the other hand, there have been only a few studies using rosin for epoxy resin applications. In one study, rosin-based polyamides were synthesized and used as hardeners for epoxy resins.[12] In another study, glycidyl esters of maleopimaric acid were prepared and then the resulting epoxides were cured with 1,2-cyclohexanedicarboxylic anhydride.[13] However, the relatively low hydrolysis resistance and thermal stability of the ester linkages in the epoxy resin may limit its application in uses such as electronics packaging.

It is known that anhydride-type curing agents are widely used for epoxy coating resins. Maleopimaric acid has similarities in rigid structure and functionality to trimellitic acid which is an important building block for anhydride-type curing agents. Since the conjugated carbon–carbon double bond in levopimaric acid can easily undergo Diels–Alder reaction with maleic anhydride, we are more interested in using maleopimaric acid derivatives as curing agents. Although only levopimaric acid possesses the optimum cyclic diene structure for Diels–Alder addition, the other isomeric rosin acids can undergo isomerization to levopimaric acid at elevated temperatures, preferably in the presence of a strong acid.[3] Considering that the ether group is more hydrolytically and thermally stable than the ester group, derivatives of rosin-based glycidyl ether are preferred for the preparation of rosin-based epoxies.

In this study, two model compounds, which represented rosin-based anhydride type curing agents and rosin-based glycidyl

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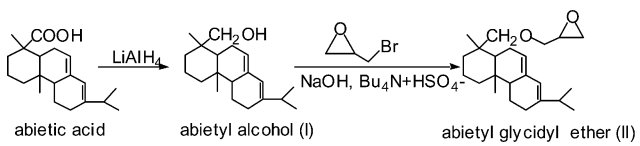
ether type epoxies, respectively, were prepared. The respective curing reactions of the epoxide with aniline and the anhydride with phenyl glycidyl ether and cure kinetics were also investigated. To the best of our knowledge, there has not been a similar study using glycidyl ether of rosin analogs as epoxies and maleated rosin analogs as hardeners in the literature. This study is part of the results from our recent investigation utilizing rosin acids as building blocks for epoxies and hardeners. The major aim of this study is to provide some synthesis methods for rosin-based anhydride and glycidyl ether and to investigate their curing and cure reactions in potential epoxy applications.

Results and discussion

Synthesis of model compounds

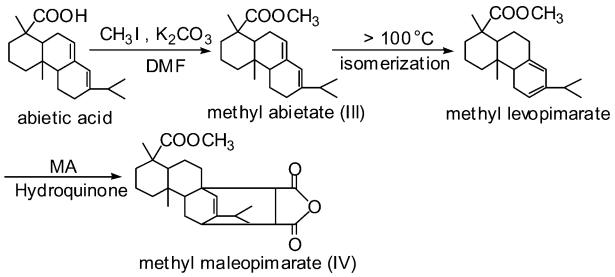
Maiti *et al.*[2] and Vandenberg[14] reported the preparation of epoxy resins-based on glycidyl esters of rosin or rosin derivatives in the literature. Those epoxides were prepared by the reaction between the carboxyl groups of rosin or the anhydride groups of maleated rosin with epihalohydrin. However, those epoxies contained ester linkages rather than ether linkages between the rosin moiety and the glycidyl groups. Considering that the ether linkage is more resistant to hydrolysis and thermolysis than the ester group, the glycidyl ether type of rosin-based expoxies is more advantageous. In this study, the glycidyl ether of abietic alcohol was synthesized as an analog to rosin-based epoxies. The carboxyl group of rosin acid was first reduced to a hydroxyl group which was then reacted with epihalohydrin to achieve the glycidyl ether.

To reduce the carboxyl group of rosin to a hydroxyl group, $LiAlH_4$ was used as the reducing agent (Scheme 1). The resulting abietyl alcohol intermediate (**I**) was then reacted with epibromohydrin to form abietyl glycidyl ether (**II**) in the presence of a phase transferring catalyst $Bu_4N^+HSO_4^-$. Because of the steric hindrance effect of the fused ring on the hydroxyl methyl group of abietyl alcohol, using epichlorohydrin only resulted in a very low yield of the glycidyl ether. By using the more reactive epibromohydrin, the etherification was able to proceed with a better yield. The yield and recovery yield of the epoxide from the two-step reaction were 29% and 87%, respectively.



Scheme 1 Synthesis route of abietic glycidyl ether.

For the preparation of an analog to the rosin-based anhydride hardeners, the free carboxyl groups of rosin were first blocked by esterification (Scheme 2) with CH_3I in DMF, using K_2CO_3 as the catalyst. Similar to the above etherification, the fused ring also had a significant steric hindrance effect on the reaction of the carboxyl group. Employing other reagents, such as methanol/*p*-toluenesulfonic acid, methanol/KOH, and methanol/*N*,*N*′-dicyclohexyl-carbodiimide, did not yield satisfactory results. Maleic anhydride was added onto the methyl ester of abietic acid (**III**) through Diels–Alder reaction, using hydroquinone as the catalyst. It was known that levopimaric acid was the only



Scheme 2 Synthesis route of methyl maleopimarate.

rosin acid which could undergo Diels–Alder adduction, and the other isomeric rosin acids experienced the isomerization to levopimaric acid at elevated temperatures during the reaction.[2,3] The yield of rosin-based anhydride (**IV**, methyl maleopimarate) from the two-step reaction was 66%. Using H_3PO_4 as a catalyst in the Diels–Alder reaction could also achieve the final product, but resulted in a lower yield (54%) from the two-step reaction. The structures of the intermediate and final products were identified by ^{1}H NMR. Fig. 1 gives the ^{1}H NMR spectra of abietic acid, abietyl glycidyl ether and methyl maleopimarate. Chemical shift peaks from δ 0.6 to 2.2 were attributed to the protons of six-member fused rings of rosin.

Curing and cure kinetics

Similar to the isothermal curing of many other epoxy systems, a reaction was noted to take place during heating to the selected cure temperatures in this study. Although approaches such as dropping the cold sample into a preheated DSC or curve fitting could be adopted to compensate for the lost signal,[15] in this study we selected the simple nonisothermal method for the curing study. It has been concluded that there is no fundamental contradiction between kinetic parameters determined from isothermal and nonisothermal experiments,[16,17] though the inconsistency in Arrhenius parameters between these two methods persists.[18,19] Fig. 2 shows the exothermic heat flows of nonisothermal curing of the model compounds in the DSC experiment. The DSC experiment results are summarized in Tables 1 and 2. As the heating rate (β) increased, initial curing temperature (T_i), peak exothermic temperature (T_p) and temperature at curing end (T_e) all shifted to higher temperatures, and the range of curing temperature widened. However, the curing time actually decreased with heating rate increase. The enthalpy of cure reaction generally increased with heating rate up to 10 °C min^{-1}, then showed a significant decrease at 20 °C min^{-1}.

While the shift in the cure temperature of the cure reaction with heating rate is more probably methodological, the dependence of the cure reaction enthalpy on heating rate is supposed to have a chemical nature.[20] Epoxy curing involves a sequence of elementary reactions; these elementary steps and reaction pathway are temperature dependent. The relatively low enthalpy at heating rate 20 °C min^{-1} for both curing systems is likely related to the different reaction pathways involved at the higher cure temperature. DSC analysis measures the overall reaction enthalpy. Without a comprehensive analysis of the possible elementary reactions, DSC results can only provide very limited information on the cure mechanism. Nevertheless,

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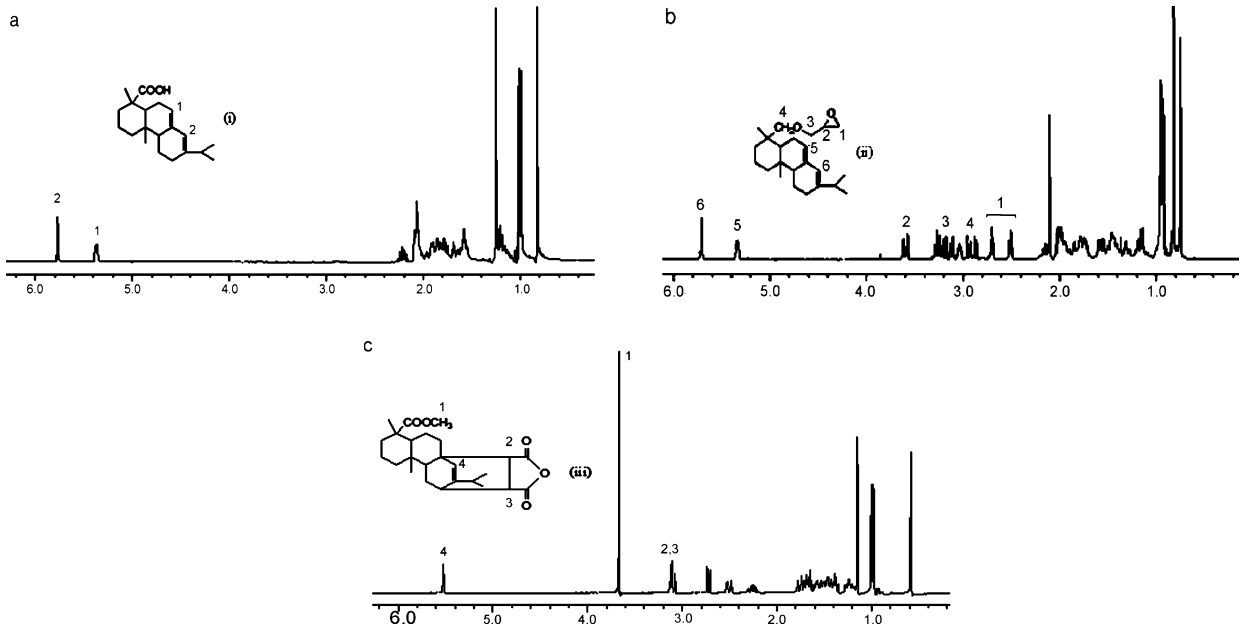

Fig. 1 ^{1}H NMR spectra of (a) abietic acid, (b) abietyl glycidyl ether, (c) methyl maleopimarate.

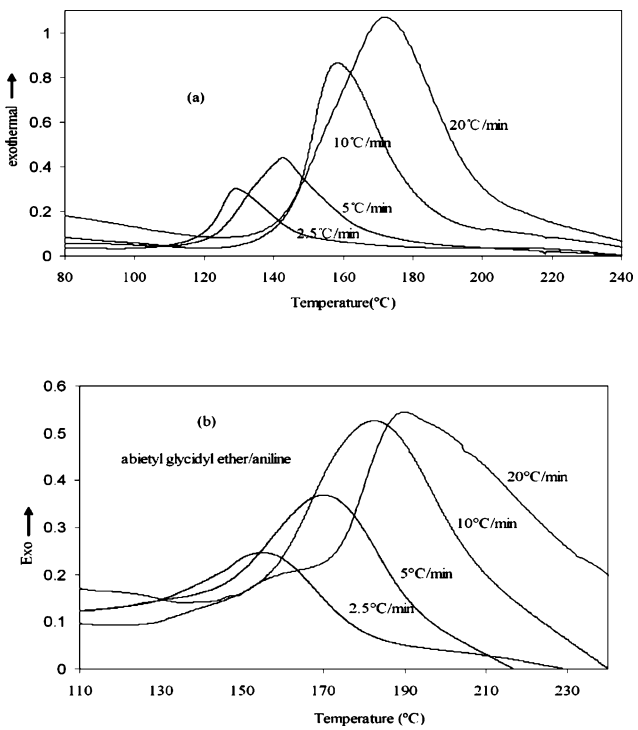

Fig. 2 DSC thermograms of curing of model compounds at different heating rates.

Table 1 DSC results of nonisothermal curing of the methyl maleopimarate/phenyl glycidyl ether system

20	112.4	80.4	411.8	444.2	499.5
10	151.8	108.5	406.7	430.8	505.8
5	128.4	91.8	390.1	415.3	457.8
2.5	139.6	99.8	380.9	402.1	451.4
0[b]	127.9[c]	91.5[c]	392	402	422

[a] On the basis of per mole of epoxide. [b] Linear extrapolation at $dT/dt = 0$. [c] Enthalpy was extrapolated by excluding the result at a heating rate of 20 °C min^{-1}.

Table 2 DSC results of nonisothermal curing of the abietyl glycidyl ether/aniline system

β/K min^{-1}	ΔH/J g^{-1}	ΔH/kJ mol^{-1}[a]	T_i/K	T_p/K	T_e/K
20	55.4	21.6	423.0	463.2	516.6
10	105.5	41.2	408.7	455.1	491.8
5	93.5	36.5	394.5	443.9	463.5
2.5	90.3	35.3	382.7	429.2	444.6
0[b]	105[c]	41[c]	397	431	448

[a] On the basis of per mole of epoxide. [b] Linear extrapolation at $dT/dt = 0$. [c] Enthalpy was extrapolated by excluding the result at a heating rate of 20 °C min^{-1}.

the dependence of cure kinetics on heating rate could be eliminated by extrapolating the results to infinitely slow heating rates (isothermal conditions), therefore "true" cure reaction temperature and Arrhenius parameters can be determined.[18] The values of these curing reaction parameters at the zero heating rate were estimated from linear extrapolation and are also given in Tables 1 and 2, ranging from 119 to 149 °C for maleopimarate/EPP and from 124 to 175 °C for abietyl glycidyl ether/aniline, respectively. If the initial curing, peak and curing end temperatures at the zero heating rate can be used as references for the selection of temperatures in the isothermal curing study,[20,22] then these temperatures fell within the conventional epoxy curing temperature range. By comparing the enthalpy of the cure reaction on the basis of per mole of epoxide, it was interesting to note that the molar enthalpy of curing of abietyl glycidyl ether by aniline (~33 kJ mol^{-1}) was less than half of that of the curing of the phenyl glycidyl ether system. The latter showed a molar enthalpy of reaction (~ 91 kJ mol^{-1}) close to that of diglycidyl ether of bisphenol A cured with *m*-phenylene diamine.[20,21] This result suggests that

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rosin-based epoxy tends to yield significantly lower enthalpy of reaction than the conventional epoxies.

Fig. 3 shows the progress of reaction conversion with curing temperature. The s-shaped curves of degree of conversion (α) *versus* temperature indicate that the cure reaction was autocatalytic.[23] The slope reached a maximum in the range of low to medium conversions. This is a clear indication that the reaction intermediates accelerated the cure reaction. At higher conversions, the linearity is lost, indicating the decrease in reaction rate. Since there was no network structure formed in the model reaction systems, the slowdown of reaction in this region was probably due to the decrease in the reactant concentrations. Fig. 4 shows the cure rate as a function of curing temperature. It indicates that the maximum reaction rate occurred around the peak exothermic temperature, and increased with heating rate.

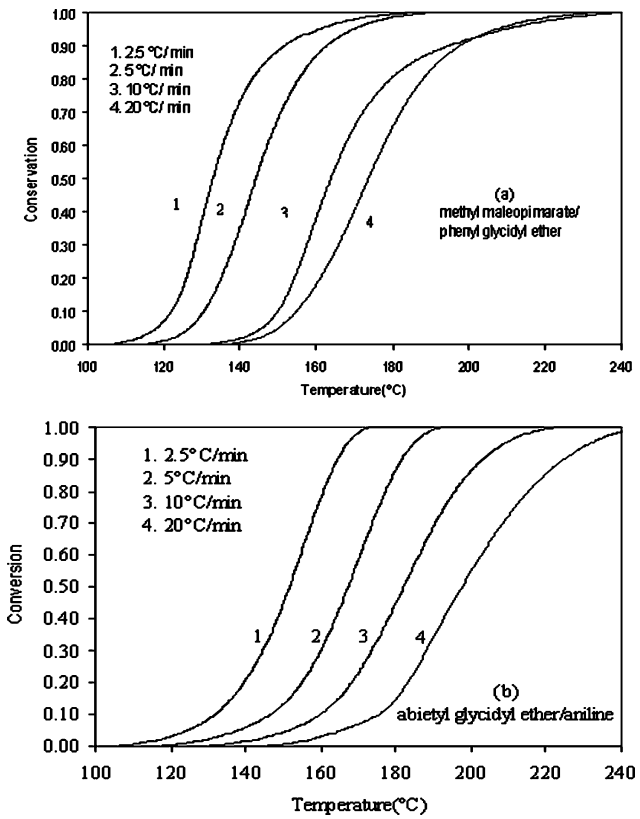

Fig. 3 Degree of conversion *versus* temperature at different heating rates.

Activation energy was measured following the Kissinger's method:[24]

$$E_a = -R\left[\frac{\mathrm{d}(\ln \frac{\beta}{T_p^2})}{\mathrm{d}(1/T_p)}\right]$$

where β = heating rate; T_p = peak exothermic temperature (K); E_a = kinetic activation energy; and R = gas constant (1.987 cal K^{-1} mol^{-1}). The plot of $\ln(\beta/T_p^2)$ against $1/T_p$ fell in a good linear relationship (curves not shown), and the slope was equal to $-E_a/R$. The calculated value of E_a was 65.3 ± 4.8 kJ mol^{-1} for the methyl maleopimarate/1,2-epoxy-3-phenyl propane system and 91.6 ± 5.2 kJ mol^{-1} for the abietyl glycidyl ether/aniline system, respectively.

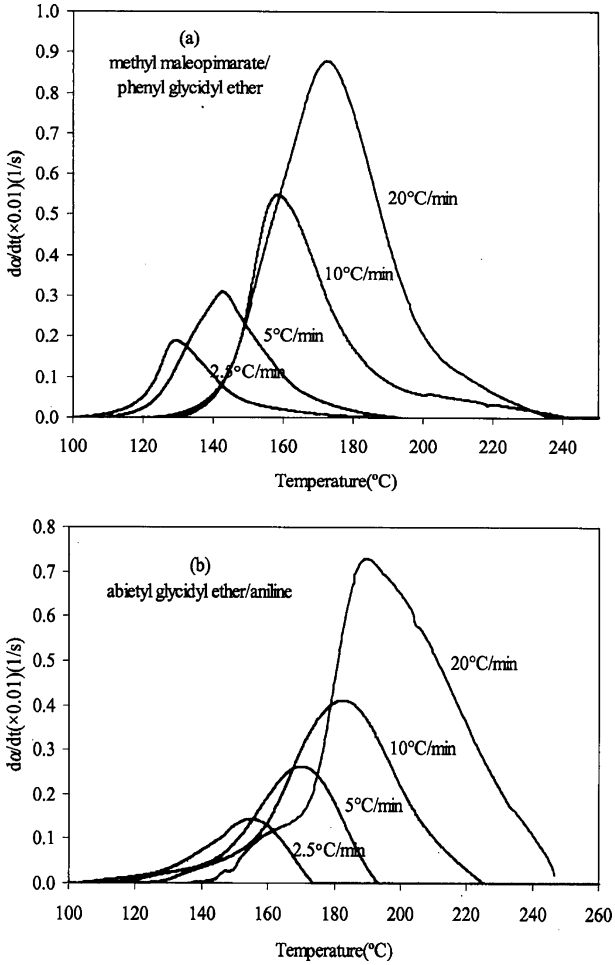

Fig. 4 Effect of heating rate on reaction rate.

Cure reactions and curing mechanism

The reactant mixture before curing and the product after curing were analyzed by ^{1}H NMR. Fig. 5 shows ^{1}H NMR spectra of the above two reaction systems before and after curing. The cured products in Fig. 5 were from the above nonisothermal DSC curing study at a heating rate at 2.5 °C min^{-1}. The assignments of the chemical shifts correspond to those labels in Scheme 3. The chemical shifts of the oxirane in phenyl glycidyl ether at δ 2.77, 2.91 and 3.36 (Fig. 5a) basically disappeared after the cure reaction with methyl maleopimarate; instead, new peaks at δ 3.65 and δ 5.35, which were attributed to the methylene and methenyl groups connected with the newly formed ester and hydroxyl groups (Scheme 3a), respectively, were observed. The peaks at δ 3.97 and δ 4.16 were attributed to the diastereomeric protons of the methylene connecting with the oxirane, and disappeared after curing. Chemical shifts of the double bond (δ 5.53), methyl group (δ 3.67) of the rosin ester and other protons in the rosin moiety did not show any observable changes.

In the abietyl glycidyl ether/aniline reaction system (Fig. 5b), the peaks at δ 2.57, 2.76 and 3.65, which were attributed to

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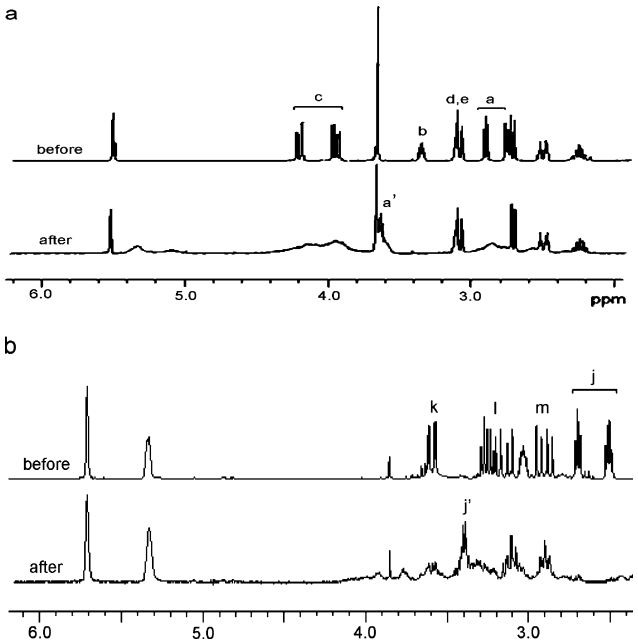

Fig. 5 ^{1}H NMR spectra before and after curing reaction. a: methyl maleopimarate/1,2-epoxy-3phenoxy propane; b: abietyl glycidyl ether/aniline.

the oxirane, disappeared after reaction. A new peak at 3.40 attributed to the methylene group connected with aniline was noted. Similarly, the chemical shifts at δ 5.71 and 5.32, which belonged to the two protons of the two double bonds in the rosin structure, and the chemical shifts of other protons in the rosin moiety did not change after curing.

Based on the ^{1}H NMR results of cure reactions, the curing mechanisms for the two epoxy systems in this study can be suggested as in Scheme 3. In the presence of a base catalyst (2-ethyl-4-methyimidazole), rosin-based anhydride curing of epoxide selectively resulted in the formation of diester (Scheme 3a), and this result was consistent with the well established epoxy curing mechanisms using anhydride.[25] Initially the catalyst activated the reaction by attacking the oxirane, forming a hydroxyl-containing intermediate (**I**).[26] This intermediate reacted with the rosin-based anhydride to yield a monoester with a free carboxyl group, which then reacted with an epoxide to form a diester with a hydroxyl. The reaction continued in the same cycle. The cure reactions of rosin-based epoxy with aniline were also suggested as in Scheme 3b. According to Shechter *et al.*,[27,28] a primary and a secondary amine reacted with epoxide to give a secondary and a tertiary amine, respectively. Without more evidence, the involvement of the catalyst in the curing of the abietyl glycidyl ether/aniline system was not discussed in this study. There was no evidence of reaction (etherification) between epoxide and the newly formed hydroxyl groups noted. This was probably due to the equivalent stoichiometric amount of reactants used in the reaction system, where excess epoxide was not available for favorable etherification. In this study, under the condition of 1 : 1 epoxy/anhydride (or 1 : 1 epoxy/amine) equivalent stoichiometry, the reaction selectively resulted in a hydroxyl ester or tertiary amine rather than polyether. In addition, according to Shechter *et al.*,[25] the esterification is the preferred reaction in a base-catalyzed system.

Conclusions

Rosin acid derivatives, glycidyl abietyl ether and methyl maleopimarate, were successfully synthesized as analogs for rosin-based epoxies and anhydride curing agents, respectively. The synthesis methods for the products and intermediates were examined in detail. The maleation of methyl abietate was relatively easy and gave a good yield, while the etherification of the abietic alcohol showed steric hindrance as reflected in the relatively low yield. The nonisothermal curing study by DSC suggested that both the curing reaction of epoxide with the rosin anhydride compound and the curing reaction of rosin epoxide with aniline were autocatalytic, and the cure reactions were similar to the respective conventional epoxy resin systems. In the presence of 2-methy-4-ethyl-imidazole catalyst and under the equivalent stoichiometric amount of epoxy and curing agent, the curing of rosin-based anhydride with 1,2-epoxy-3phenoxy-propoane selectively yielded a diester, and the curing of rosin-based epoxy cured with aniline selectively yielded a tertiary amine. There was no etherification noted in the cure reactions.

Experimental

General

Abietic acid (75% by HPLC) was obtained from Aldrich and used as received. It was actually a mixture of abietic acid and other rosin acids with the most neutral rosin compounds removed. Maleic anhydride (powder, 95%), iodomethane (99.5%), epibromohydrin (98%), hydroquinone (99%), phenyl glycidyl ether (99%) and 2-ethyl-4-methylimidazole (95%), aniline (99.5%) were also obtained from Aldrich. Lithium aluminum hydride (95%) was obtained from ACROS. Tetra-n-butylammonium hydrogen sulfate (97%) was obtained from Lancaster. Sodium hydroxide (99%, pellet), potassium carbonate (99%, anhydrous, granular) were obtained from B.T. Baker. Magnesium sulfate (anhydrous, reagent grade) was obtained from Fisher, as were all organic solvents (analytical grade). Solvents for synthesis (methanol, xylene, toluene, THF, DMF) were dried with 5 Å molecular sieves before use; the others (ethyl ether, chloroform) were used as received. TLC was performed on silica gel/UV_{254} (0.25 mm, Sorbent Technology) plates. Column chromatography was carried out with Merck Kieselgel 60 (0.040–0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 300 MHz spectrometer at room temperature in deuterated chloroform ($CDCl_3$). Chemical shifts are reported relative to chloroform (δ 7.26) for ^{1}H NMR and chloroform (δ 77.28) for ^{13}C NMR. FTIR spectra were recorded with NEXUS 670 FT-IR, KBr pellet, wavelength from 4000 to 400 cm^{-1}. Mass spectrum was recorded with a LCQ Advantage ESI mass spectrometer.

Synthesis of model compounds

Abietyl alcohol (I). Abietic acid (2.00 g, 75% purity, 5 mmol) in dry THF (60 mL) was added dropwise to a suspension of powdered $LiAlH_4$ (1.12 g, 29.4 mmol) in dry THF (30 mL) at room temperature. The reaction mixture was stirred overnight at room temperature. To this mixture was added 60 mL water and 50 mL H_2SO_4 (1 M), stirring for 1 h. The mixture was extracted

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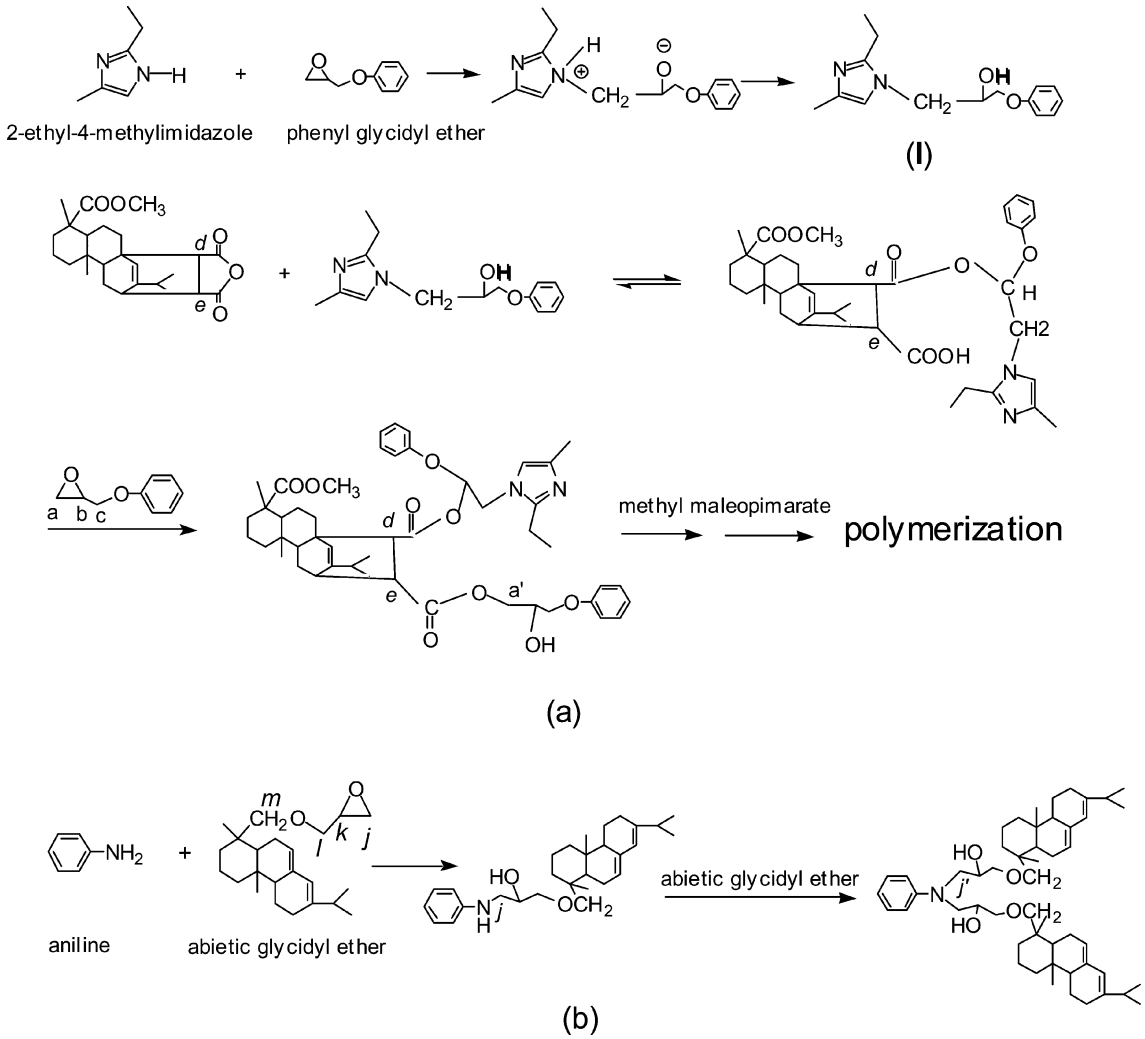

Scheme 3 Curing reactions of methyl maleopimarate/phenyl glycidyl ether (a), and abietyl glycidyl ether/aniline (b).

with ethyl ether (60 mL × 3). After drying with anhydrous $MgSO_4$ and evaporating the solvent, the residue was purified by silica gel column chromatography (AcOEt : hexane = 13 : 87) to yield the product (**I**, 1.38 g, yield 96.5%). ^{1}H NMR δ 5.77 (s,1H), 5.40 (s,1H), 3.36 (m,1H), 3.13 (m,1H), 2.17–1.83 (m,9H), 1.37–1.22 (m,5H), 1.03–1.01 (m,7H), 0.75–0.41 (m,7H). ^{13}C NMR δ 145.47, 135.77, 122.60, 121.13, 72.35, 50.99, 43.88, 39.09, 37.72, 35.93, 35.11, 34.86, 27.75, 24.05, 22.90, 21.66, 21.10, 18.40, 17.93, 14.47. FT-IR ν 889, 1050, 1300, 1380, 1470, 2960, 3390 cm^{-1}. ESI-MS m/z 289.2, [M + H$^+$].

Abietyl glycidyl ether (II). Abietic alcohol (**I**) (527 mg, 1.8 mmol) was dissolved in toluene (10 mL) at room temperature. To this solution were added powdered NaOH (146 mg, 3.6 mmol) and $Bu_4N^+HSO_4^-$ (186 mg, 0.5 mmol). The mixture was stirred for 0.5 h at room temperature and then epibromohydrin (600 mg, 4.4 mmol) was dropped in. The mixture was further stirred overnight at 60 °C and cooled to room temperature. The reaction was quenched with H_2O (20 mL) and the mixture was extracted with ethyl ether (30 mL × 3). After drying with anhydrous $MgSO_4$ and removing the solvent under reduced pressure, the product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 9). [**II**, 200 mg, yield 30% (yield based on recovering start material 90%)]. ^{1}H NMR δ 5.77 (s,1H), 5.40 (s,1H), 3.65 (m,1H), 3.36–2.92 (m,4H), 2.76 (m,1H), 2.57 (m,1H), 2.21–1.20 (m,12H), 1.02–0.98 (m,8H), 0.88–0.81 (m,7H). ^{13}C NMR δ 145.16, 135.42, 122.44, 121.24, 80.92, 72.03, 51.08, 50.69, 44.24, 43.89, 38.80, 37.25, 36.37, 34.88, 34.63, 27.54, 23.99, 22.66, 21.42, 20.86, 18.22, 18.03, 14.23. FT-IR ν 768, 883, 893, 922, 1110, 1260, 1380, 1470, 1740, 2960 cm^{-1}. ESI-MS m/z 345.2, [M + H$^+$]; 367.2, [M + Na$^+$].

Methyl abietate (III). Powdered K_2CO_3 (5.75 g, 42 mmol) was added to anhydrous DMF (60 mL) and the mixture was stirred for 5 min at 25 °C. To this mixture was added abietic acid (5.00 g, 75% purity, 12 mmol) and then iodomethane (11.40 g, 60 mmol). The reaction was stirred for 4 h at 25 °C and the solid precipitate was removed *via* filtration. The filtrate was diluted with 300 mL ethyl ether, and then washed with water (3 × 100 mL). The ethyl ether layer was then dried with anhydrous $MgSO_4$ and concentrated in vacuum. Purification was carried out by silica-gel column chromatography (EtOAc : hexane = 1 : 9) to provide methyl abietate (**III**, 3.00 g, yield 77%). ^{1}H NMR δ 5.77 (s,1H), 5.36 (s,1H), 3.62 (s,3H), 2.23–1.56 (m,11H),

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1.25–1.18 (m,6H), 1.02–1.00 (m,7H), 0.80 (s,3H). ^{13}C NMR δ 179.20, 145.52, 135.74, 122.56, 120.84, 52.06, 51.15, 46.81, 45.32, 38.55, 37.33, 35.11, 34.75, 27.70, 25.90, 22.69, 21.64, 21.08, 18.36, 17.24, 14.26. FT-IR ν897, 1150, 1230, 1250, 1390, 1460, 1730, 2960 cm^{-1}. ESI-MS m/z 317.6, [M + H$^+$]; 339.6, [M + Na$^+$].

Methyl maleopimarate (IV). Methyl abietate (**III**) (3.00 g, 9 mmol), maleic anhydride (1.76 g, 18 mmol) and hydroquinone (0.02 g, 0.18 mmol) were mixed in a sealed tube in dry xylene (10 mL). The mixture was stirred at 220 °C for 5 h under Ar protection. The reaction was cooled to 80 °C, and the reaction solution was transferred into a beaker. Most of the product precipitated itself as crystals with the cooling down of the solution and was collected with a funnel. The residual product in the filtrate was precipitated with ethyl ether (50 mL) and collected by filtration. Then the two solid parts were combined and washed with 200 mL ethyl ether, dried to obtain the pure product (**IV**, 3.2 g, yield 86%). ^{1}H NMR δ 5.53(s,1H), 3.67 (s,3H), 3.11 (m,2H), 2.72 (d,1H), 2.50 (m,1H), 2.25 (m,1H), 1.78–1.24 (m,13H), 1.15 (s,3H), 1.00–0.98 (d,6H), 0.59 (s,3H). ^{13}C NMR δ 179.32, 172.97, 171.26, 148.31, 125.34, 53.51, 53.47, 52.27, 49.64, 47.30, 45.87, 40.67, 38.21, 37.89, 36.90, 35.88, 35.00, 32.99, 27.42, 21.85, 20.79, 20.17, 17.20, 16.95, 15.76. FT-IR ν 795, 850, 922, 945, 1000, 1090, 1140, 1240, 1390, 1470, 1720, 1790, 1860, 2880, 2960cm^{-1}. ESI-MS m/z 415.4, [M + H$^+$].

Sample preparation for curing study

To study the curing activity of methyl maleopimarate (MMAP), phenyl glycidyl ether (PGE) was used as the epoxide. In order to achieve a good mixing of the reactants, MMAP/PGE in molar ratio 1 : 2 together with the catalyst were first dissolved in $CHCl_3$, and then the solvent was removed in a vacuum at room temperature. To study the curing activity of abietyl glycidyl ether (AGLE), aniline was used as the curing agent. Similarly, an equivalent stoichiometric amount of AGLE and aniline (AGLE/aniline in molar ratio 2 : 1) together with a catalyst were first dissolved in ethyl ether, and then the solvent was removed in vacuum at room temperature. For both epoxy systems, 2-ethyl-4-methylimidazole was added as a catalyst during preparation at the level of 0.5 wt% of the total weight of epoxide and curing agent. The mixtures were sealed in glass vials and were kept in dry ice for a maximum of 48 h while waiting for curing tests.

Curing study by DSC and ^{1}H NMR

Nonisothermal curing of the epoxy systems was performed on a Mettler-Toledo 822e DSC in a nitrogen atmosphere. Heat scan ranging from −50 to 250 °C was performed at heating rates of 2.5, 5, 10, and 20 °C min^{-1}, respectively. Approximate 5 mg of each of the above prepared samples was weighed and sealed in an aluminium DSC sample pan, and the curing was conducted immediately. The degree of conversion of the epoxy group at any instantaneous temperature (or time) during the curing reaction, α, was calculated from the area under the DSC exothermic peak:

$$\alpha = \frac{Q_t}{Q_{\text{tot}}}$$

where Q_t was given by the fraction peak area at time t (or corresponding temperature T) and Q_{tot} by the total peak area.

The cure reactions were studied by ^{1}H NMR analysis of the reaction products. The reacted sample after curing on DSC and unreacted samples were examined using ^{1}H NMR in $CDCl_3$.

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References

1 J. J. W. Coppen and G. A. Hone, *Gum naval stores: Turpentine and rosin from pine resin*, Food and Agriculture Organization of the United Nations, 1995, ch. 1.
2 S. Maiti, S. S. Ray and A. K. Kundu, *Prog. Polym. Sci.*, 1989, **14**, 297–338.
3 S. Das and S. Maiti, *J. Macromol. Sci., Chem.*, 1982, **A17**, 1177–1192.
4 S. S. Ray, A. K. Kundu, M. Ghosh and S. Maiti, *Eur. Polym. J.*, 1985, **21**, 131–133.
5 S. S. Ray, A. K. Kundu and S. Maiti, *J. Appl. Polym. Sci.*, 1988, **36**, 1283–1293.
6 J. B. Lewis and G. W. Hederick, *Ind. Eng. Chem. Prod. Res. Dev.*, 1970, **9**, 304–310.
7 Y. Zhang and D. J. Hourston, *J. Appl. Polym. Sci.*, 1998, **69**, 271–291.
8 J. F. Jin, Y. L. Chen, D. N. Wang, C. P. Hu, S. Zhu, L. Vanoverloop and D. Randall, *J. Appl. Polym. Sci.*, 2002, **84**, 598–604.
9 S. S. Roy, A. A. Kundu and S. Maiti, *Eur. Polym. J.*, 1990, **26**, 471–474.
10 X. Liu, C. Li, D. Zhang, Y. Xiao and G. Guan, *Polym. Int.*, 2006, **55**, 545–551.
11 X. Liu, C. Li, D. Zhang and Y. Xiao, *J. Polym. Sci., Part B: Phys.*, 2006, **44**, 900–913.
12 A. M. Atta, R. Mansour, M. I. Abdou and A. M. Sayed, *Polym. Adv. Technol.*, 2004, **15**, 514–522.
13 T. Matynia, *J. Appl. Polym. Sci.*, 1980, **25**, 1–13.
14 E. J. Vandenberg, *US Pat.*, 3 285 870, 1966.
15 R. B. Prime, in *Thermal characterization of polymer Materials*, ed. E. Turi, Academic Press, San Francisco, 1997, vol. 2, ch. 6, pp. 1389–1400.
16 H. J. Flammersheim, *Thermochim. Acta*, 2000, **361**, 21–29.
17 J. Sestak, in *Comprehensive analytical chemistry*, ed. G. Svehla, Elsevier, Amsterdam, 1976, vol. 12D, ch. 9, pp. 212–217.
18 S. Vyazovkin and C. A. Wight, *Annu. Rev. Phys. Chem.*, 1997, **48**, 125–49.
19 S. Vyazovkin and N. Sbirrazzuoli, *Macromol. Chem. Phys.*, 1999, **200**, 2294–2303.
20 V. L. Zvetkov, *Polymer*, 2001, **42**, 6687–6697.
21 Z. Dai, Y. Li, S. Yang, C. Zong, X. Lu and J. Xu, *J. Appl. Polym. Sci.*, 2007, **106**, 1476–481.
22 S. Sourour and M. R. Kamal, *Thermochim. Acta*, 1976, **14**, 41–59.
23 D. K. Hadad, in *Epoxy resins chemistry and technology*, ed. C. A. May, Marcel Dekker, Inc., New York and Basel, 2nd edn, 1988, ch. 14, pp. 1127–133.
24 H. E. Kissinger, *J. Res. Natl. Bur. Stand.*, 1956, **57**, 217–221.
25 L. Shechter and J. Wynstra, *J. Ind. Eng. Chem.*, 1956, **48**, 86–93.
26 T. Dearlove, *J. Appl. Polym. Sci.*, 1970, **14**, 1615–1626.
27 L. Shechter, J. Wynstra and R. P. Kurkjy, *J. Ind. Eng. Chem.*, 1956, **48**, 94–97.
28 L. Shechter, J. Wynstra and R. P. Kurkjy, *J. Ind. Eng. Chem.*, 1957, **49**, 1107–1109.

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