

Biobased Epoxy Resin from Canola Oil

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ABSTRACT: Epoxidized canola oil (ECO)-based thermoset epoxy resins were formulated with phthalic anhydride (PA) as the curing agent for different ratios of ECO to PA (1:1, 1:1.5, and 1:2 mol/mol) at curing temperatures of 155, 170, 185, and 200°C. The gelation process of the epoxy resins and the viscoelastic properties of the systems during curing were studied by rheometry, whereas the dynamic mechanical and thermal properties of the cured resins were studied by dynamic mechanical analysis (DMA) and differential scanning calorimetry. We found that the thermomechanical properties of the resins were not strongly dependent on the curing temperature of the resin, although elevated temperatures significantly accelerated the curing process. However, an increase in the curing agent (PA) amount significantly altered both the reaction rate and the thermomechanical properties of the final resin. Thus, in the ECO/PA system, the selection of the combination of the curing temperature and the molar ratios of the curing agent could be used to design thermoset resins with unique thermomechanical properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40142.

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INTRODUCTION

Epoxy resins are an important class of materials, which are used widely in electrical, automobile, and other applications because of their excellent chemical resistance, outstanding adhesion to a variety of substrates, high tensile and compressive strengths, electrical insulation properties, and superior fatigue strength.^{1–3} Common applications for epoxy resins were reviewed in detail elsewhere.² Linear or crosslinked epoxy polymers are obtained by the reaction of epoxy monomers with curing agents (hardeners) and/or initiators. Mechanisms for the polymerization of epoxy monomers to form crosslinked polymers via step polymerization, chain polymerization or a combination of mechanisms were reviewed earlier.³ Epoxy groups can react with many functional groups, including amines, phenols, mercaptans, isocyanates, and acids.^{2,3} Typically, the concentration of epoxy groups in the epoxy monomer used is approximately equal to the concentration of reactive groups in the hardener/initiators because, under these conditions, unwanted side reactions are minimized. Crosslinked epoxy resins are cohesively very strong, but their brittleness reduces their usefulness in many applications, especially those requiring a high impact strength. Hence, the development of epoxy resins in recent years has focused on toughening. This can be achieved by the modification of the chemistry of the raw materials within the formulation⁴ or by the addition of particulates, elastomers, or thermoplastics to the formulation.²

Currently, the major components used in most epoxy-based thermoset polymer formulations originate from petroleum-based derivatives. However, resins and composites incorporating renewable resources are increasingly being used in diverse areas of manufacturing because of the heightened awareness of environmental issues. To date, these biobased resins only represent a very small percentage of the entire plastics market, and the widespread application of biobased materials is still limited by the available materials plus their cost of production. Hence, the development of cost-effective biobased materials from abundantly available renewable sources is of great interest to prevent reliance on finite petroleum resources.

For example, processes for creating biobased polyols from vegetable oils have been described in the literature^{5–7} as have some of the challenges in making biobased polymers from such renewable resources.⁸ A comparison of the life cycles and the environmental impact of soy- and petro-based polyols has also been discussed.⁹ Usually, vegetable-oil-based polyol synthesis is a two-step process, in which the first step is the epoxidation of unsaturated vegetable oil fatty acids or fatty esters.^{10–13} The second step of the process is the subsequent reaction of the epoxy groups, which usually involves two or more hydroxyl-group-containing reactants and acid catalysts.^{11,14–16} In addition to their broad applications in the making of polyols, biobased-epoxy-resin-epoxidized vegetable oils can also be used in similar

ways as petrochemical epoxy derivatives. These applications include the use of biobased epoxies as additives in specialty coatings and as plasticizers,¹⁵ as interfiber bonding adhesives in glass^{15,17} and lignocellulosic¹⁷ composite materials, and in the automobile industry.¹⁸

Epoxy resins are most usually cured with primary or secondary amines to form thermoset polymers. However, it is known that the use of anhydrides in the curing reactions of epoxies may also lead to similar thermoset resins, although the curing reaction must usually be carried out at elevated temperatures. Anhydride-cured epoxy resins often serve as matrices for advanced, fiber-reinforced composites used in a variety of aerospace, structural, and sporting applications, where their high specific strength and stiffness combined with their good thermal stability offer unique design advantages.¹⁹

Most commonly, vegetable oil epoxide based materials with commercial applications have been made from epoxidized soybean oils (ESOs). For example, ESO is used as plasticizer or stabilizer to modify the properties of plastic resins such as thermoplastic poly(vinyl chloride).²⁰ Some researchers have also investigated the curing process of ESO with anhydrides²¹ and the conversion of the ESO into flexible, semiflexible, or rigid crosslinked thermoset polymers using various approaches.^{22,23} However, so far, the applications of plant-oil epoxy precursors are still limited because of their low crosslinking density and mechanical performance and their cost of manufacturing relative to that of petrochemical epoxides. The development of alternatives to petroleum-based epoxy resins for commercial applications remains a challenge for the polymer and composite industries. In this study, we explored the use of epoxidized canola oil (ECO), derived from an oilseed crop widely grown in the Canadian prairie provinces, which is high in monounsaturated fatty acids and low in saturated fatty acids. Our main goals were to investigate the curing process of ECO with an anhydride, to evaluate the properties of ECO-based thermoset resins, and to assess the commercial feasibility of these resins in making cellulosic particle and fiberboards.

EXPERIMENTAL

Materials

Food-grade canola oil (Loblaws, Inc., Canada) was purchased from the local supermarket and was used as supplied. Formic acid (technical grade, $\geq 85\%$) and hydrogen peroxide (technical grade, $\geq 35\%$) were purchased from Univar Canada. Phthalic anhydride [PA; molecular weight (MW) = 148.1 g/mol, density = 1.53 g/cm³, melting point = 131°C, reagent grade, $\geq 99\%$] from Lancaster (Alfa-Aesar) was used as a curing agent. ECO was synthesized in our laboratory, as described later.

Methods

Rheological Experiments. Rheological experiments were performed with an AR2000 Advanced Rheometer (TA Instruments). All rheological experiments were carried out immediately after the prepolymer preparation process at low strain rates (1.25%) and under identical conditions. Disposable 25-mm parallel plates were used for the test geometry. Isothermal time sweep tests were performed with 25-mm disposable

parallel plates under controlled displacement at a frequency of 1 Hz and at constant temperatures of 155, 170, 185, and 200°C to follow the influence of the reaction kinetics at different temperatures on the viscoelastic properties of the materials. Rheology Advantage Data Analysis (version 5.7.0) software was used to analyze the experimental data.

Dynamic Mechanical Thermal Analysis. The dynamic mechanical thermal properties [storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$)] were measured with a DMA Q800 (TA Instruments) equipped with a liquid nitrogen cooling system in the single cantilever bending mode at a constant heating rate of 2°C/min from -100 to 100°C. The size of the test samples was about 17.5 × 11 × 4 mm³ (± 0.5 mm). The measurement of the length, width, and thickness of the specimen accuracy was ± 0.01 mm. The measurements were performed according to ASTM E 1640-09 at a fixed frequency of 1 Hz. At least two similar sized specimens prepared by the cutting of the bulk polymer sheet were obtained, and the results were averaged. The reported errors are the subsequent standard deviations. TA Universal Analysis (version 4.7A) software was used to analyze the experimental data.

Differential Scanning Calorimetry (DSC). DSC measurements were performed with a Q100 series DSC (TA Instruments) with a modulation of $\pm 1^\circ\text{C}$ every 60 s. Approximately 8.0–10.0 mg (± 0.1 mg) of the sample was placed in an aluminum pan, which was then hermetically sealed. An empty aluminum pan was used as a reference, and the experiments were performed under a nitrogen flow of 50 mL/min. The sample was transferred to the DSC cell, where it was equilibrated at -50°C for 5 min and then heated to 100°C at a constant rate of 2°C/min. The TA Universal Analysis (version 4.7A) software was used to analyze the experimental data.

Epoxidation of Canola Oil. The epoxidation of canola oil was carried out with performic acid generated *in situ* from formic acid and hydrogen peroxide. The molar ratio of canola oil to formic acid to hydrogen peroxide was 1.0:1.0:5.6. The average MW of canola oil was 885 g/mol.

Into a 22-L glass reactor (equipped with a bottom drain and a water jacket and attached to a recirculating liquid cooler), 4000 g (4.54 mol) of canola oil was added at room temperature. Hydrogen peroxide (2470 g, 35%) was loaded into the vessel, and the mixture was stirred vigorously with an overhead mechanical stirrer (350 \pm 10 rpm) to form a homogeneous mixture before we proceeded with addition of formic acid. Formic acid (246 g, 85%) was added dropwise through an addition funnel into the reactor while the reaction mixture was stirred intensively. The formic acid addition was done at a rate of 8–10 g/min to control the temperature rise due to the exothermicity of the reaction. After the addition of formic acid was complete, the temperature of the reaction was set to 50 \pm 5°C. The epoxidation process was monitored by liquid chromatography-mass spectrometry (LC-MS) and was usually complete in 48 h under the conditions described previously.

After the epoxidation process, the product was washed with an equal amount of saturated NaCl solution (~4000 mL) at least

three times. The formic acid was neutralized with a 0.6M solution of NaOH during the second and third washes. Traces of water were removed with anhydrous Na₂SO₄, and the final product was filtered through filter paper to remove NaCl or/and Na₂SO₄ particulates. The resulting ECO was a viscous product at elevated temperatures that tended to crystallize at room temperature.

Epoxy Resin Preparation. Thermoset resins based on ECO and PA were prepared above the melting point of PA at different curing temperatures. The desired amount of PA (0.05, 0.075, or 0.10 mol) was dissolved in ECO (0.05 mol) in a glass flask that was placed in an oil bath at the desired temperature (155, 170, 185, or 200°C). The mixture was thoroughly mixed by a magnetic stirrer at 500 rpm until all of the PA was melted. The prepolymer preparation time used was varied depending on the amount of PA added; it was 10 min for the ECO/PA molar ratio of 1.0:1.0, 9 min for the molar ratio of 1.0:1.5, and 8 min for the 1.0:2.0 molar ratio. The majority of the prepolymer formed in this way was transferred into a preheated Teflon mold in an oven for further curing to form sheets with a size of 100 × 100 × 5 mm³. These cured samples were later used for the dynamic mechanical analysis (DMA) and DSC measurements.

In addition to the previous treatment, about 3–4 g of the prepolymer was quickly transferred to a small glass flask and cooled down in an ice–water mixture. These small amounts of prepolymers were used for further isothermal rheological experiments. The curing of the resins in the mold was performed for 6 h at each temperature, after which the oven was turned off to allow slow cooling (~1.0–1.5°C/min) of the final product.

RESULTS AND DISCUSSION

Epoxidation of Canola Oil

The epoxidation of unsaturated fatty acids or vegetable oils with hydrogen peroxide along with acetic, sulfuric, or formic acids is a commonly used procedure that has been described well elsewhere.^{24–26} Some advantages of the use of performic acid, which is formed by the reaction of formic acid with hydrogen peroxide, for the epoxidation process of long-chain, unsaturated aliphatic compounds have been described.²⁶ For example, the formation of peracetic acid has been described as significantly slower than the formation of performic acid under moderate reaction conditions. The exothermic reaction of formic acid with hydrogen peroxide (in oleic acid at 40°C) starts immediately, and the reaction of performic acid with oleic acid is complete within 2–4 h,²⁶ whereas the reaction of peracetic acid (at room temperature) requires more than a week to finish. Thus, the epoxidation of canola oil was carried out with an *in situ* generated performic acid, as described in the Experimental section.

Because canola oil, like other natural plant oils, is predominantly comprised of triacylglycerides (TAGs) containing a distribution of fatty acid types,^{27,28} we knew that ECO would contain a distribution of epoxidized TAG species. On the basis of the known fatty acid profile of canola oil, the number of epoxide groups per TAG molecule could vary from 0 for TAG containing three saturated fatty acids to 1 for TAG with two

Table I. Expected Products and Product Yields from the Epoxidation of Canola Oil on the Basis of the Fatty Acid Distribution of Canola Oil

Expected product of canola oil epoxidation	Number of epoxy groups per TAG	Average MW (g/mol)	Expected yield (mmol/kg)
Multifunctional epoxy	9	1017	2.3
	8	1003	6.9
	7	989	35.3
	6	975	101.2
	6 (+ P)	947	2.4
	5	961	215.6
	5 (+ P)	933	10.6
	4	947	254.7
	4 (+ S)	947	3.4
Triepoxy	4 (+ P)	919	40.9
	3	933	253.0
	3 (+ S)	933	18.1
Diepoxy	3 (+ P)	905	66.5
	2 (+ P)	891	53.5
	2 (+ 2P)	863	3.6
	2 (+ S)	920	29.3
Monoepoxy	2 (+ 2S)	920	4.5
	2 (+ SP)	891	2.3
	1 (+ 2P)	849	2.4
	1 (+ SP)	877	1.2
Saturates	PPP	807	1.2
	PPS	835	6.0
	SPS	863	2.4
	SSS	892	1.1

saturated fatty acid and one monounsaturated fatty acid (most likely oleic acid) and could range up to 9 if the TAG was trilinolenin. Table I lists the most abundant TAG products from the epoxidation of canola oil, including the number of epoxide groups, the MW, and the expected yield of the epoxidized TAGs per kilogram of canola oil with the assumption of complete conversion of all double bonds to epoxide groups. The fatty acid composition of canola oil and the MW distribution of canola oil TAGs used was that reported previously.²⁸

As shown in Table I, ECO TAGs can be classified according to the number of epoxide groups per TAG molecule. In addition, for each number of epoxide groups per TAG, there may be several species that have either the same or different MWs because of the original fatty acyl substitution on the TAG. For example, the most abundant TAG, with four epoxide groups with a nominal MW of 947, arose from a TAG with no saturated fatty acids, OOL, or its isomers. In addition, a TAG with four epoxide groups with a nominal MW of 947 also arose from a TAG containing stearic acid, SLL, SOLn, or their isomers (where S represents stearic acid, L is linoleic acid, O is oleic acid, and Ln

is linolenic acid). In addition, TAG with four epoxide groups arose from palmitic acid, PLL (where P is palmitic acid), POLn, or their isomers, although these molecules had a nominal MW of 919.

Figure 1(a) shows the distribution of epoxide groups on the TAGs in ECO on the basis of the data in Table I. In Figure 1(a), TAGs with similar numbers of epoxide groups are grouped together; the group with zero epoxides per TAG contained fully saturated TAGs. The maximum distribution of the epoxide groups was between 3 and 4; this was similar to the double-bond functionality of the canola oil, which was around 3.9 per TAG.

Figure 1(b) presents the rather broad MW distribution of epoxidized TAGs that were present in ECO. The peak maximum occurred at about 933 g/mol; this was close to the MW of the epoxidized triolein (933.43 g/mol) and to the distribution average of 942 g/mol. These values were used in later calculations to formulate ECO-based thermoset resins.

Thermoset Resin Preparation

A major challenge that was encountered in the development of biobased resins based on ECO and PA was in the sample prepara-

tion procedure. ECO is clear, colorless, and viscous liquid at 40°C, but at room temperature, it gradually solidifies. In contrast, PA was purchased as irregularly shaped white flakes with a melting point of about 131°C. To prepare the thermoset resins, it was necessary to form a homogeneous mixture of these two precursors at higher temperatures (above the melting point of PA) and to maintain and control the curing process of this mixture.

Generally, the reaction of the epoxy groups with curing agents are very complex, and multiple competing reactions, such as the formation of ethers or esters, can take place,^{2,29,30} depending on the curing agents used. For example, the reaction of epoxides with anhydrides involves multistep reactions, and some important simple examples are given in Scheme 1.

In reaction A, the anhydride ring is opened by its reaction with an alcohol to form both monoester and carboxylic acid groups. In reaction B, the carboxylic group so generated then react with the epoxide; this results in the formation of an ester linkage. In reaction C, other epoxide groups react with the hydroxyl groups to produce an ether linkage;² these hydroxyl groups may be those already existing or those formed via reactions A or B. This gives rise to oligomeric structures. It is important to note that the occurrence and the rate of reactions A and B depend on the curing temperature. At low temperatures of curing, both reactions may occur at a similar rate, whereas higher cure temperatures have been shown to favor reaction B.^{2,3}

On the other hand, epoxidized vegetable oils have internal epoxide groups that are much less reactive and require different curing conditions compared to synthetic epoxides with terminal epoxide groups (e.g., glycidyl ethers).³¹ A necessary (although not sufficient) condition for the formation of an epoxy network is that at least one of the monomers involved in the reaction should have a functionality higher than two.³

Taking the previous into account, an attempt was made to prepare prepolymers of ECO at temperatures above the melting point of PA. The objective was to form a homogeneous reactive mixture that would undergo a controlled amount of

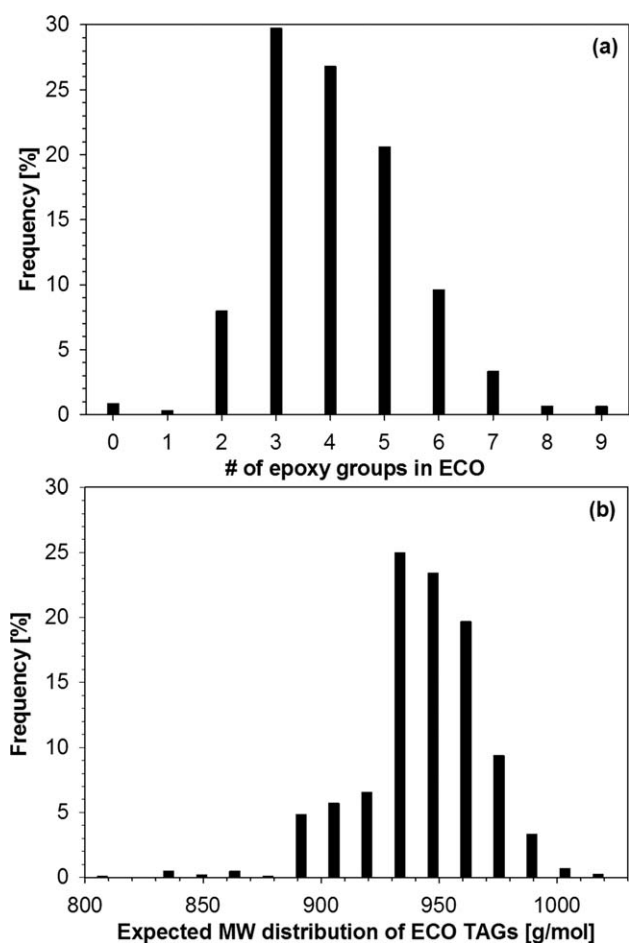
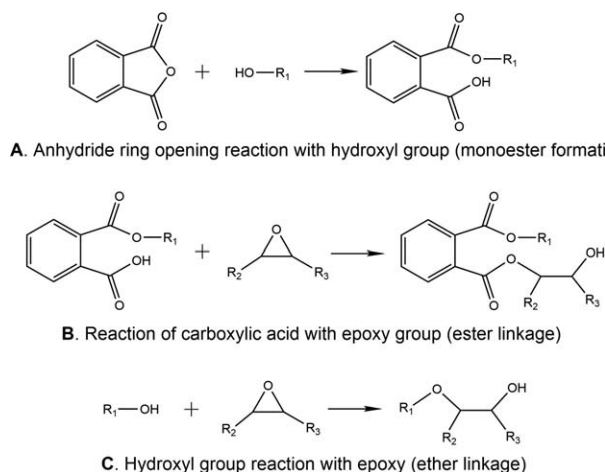


Figure 1. (a) Calculated number of epoxy groups per TAG and (b) expected MW distribution of TAGs in ECO. The epoxy number 0 corresponds to fully saturated TAGs.



Scheme 1. Important reactions of the PA and epoxy precursors occurring during the curing processes.

oligomerization via reactions such as those described in Scheme 1. This mixture could be considered to be the prepolymer preparation; further reaction could be arrested after an appropriate time (times of 8–10 min were used in this work) by shock cooling in an ice–water bath. We envisioned that this prepolymer preparation could be finally cured by its heating to a temperature most suitable for the final polymer or composite application. We recently described some aspects of the previous process for a range of biobased epoxide resin systems.²⁹

In this way, several compositions were prepared at different molar ratios of ECO to PA (1.0:1.0, 1.0:1.5, and 1.0:2.0). These particular component ratios were chosen because each PA molecule could potentially react with two epoxides.² At the same time, as described previously, on average, each molecule of epoxidized oil had about four epoxide groups. Hence, the expected stoichiometric ratio of the reactive moieties of these components was close to 1:1 at a molar ratio of ECO to PA of 1:2. These three selected compositions were each cured at four different curing temperatures above the melting point of PA: 155, 170, 185, and 200°C, as described previously in the Experimental section.

Depending on the curing conditions and the PA content, clear and transparent resins were formed; these ranged from rubberlike flexible thermosets (with low curing temperatures and low PA content) to almost rigid semiflexible plastics (with a high curing temperature and high PA content). The color of the resins varied from light yellow at low curing temperatures to yellow–light brown at higher curing temperatures.

Rheological Experiments and Gelation

Gelation is the critical transition in the formation of a network of constituent units that generates a giant macromolecular structure. It is characterized by a physical change in the reaction medium from liquid to solid where the sample viscosity tends to be infinite.³ The determination of the gelation period is a key parameter in following the curing process of the epoxy precursors; it will provide significant information on the working life (pot life) of the epoxy system.²

Rheological tools can be used to follow the gelation period of epoxy resins. Here, the change in viscosity of the epoxy resin in the early stages of curing was measured as a function of the resistance to the shear of a sample placed between two plates. However, because the gelation time may depend on the shear rate because of the shear thinning at high rates,¹⁷ all of the experiments were carried out at low strain rates (1.25%) and under identical conditions. In this way, the rheological experiments on the ECO/PA resins were carried out at different temperatures to characterize the physical transformations during the curing process. These rheological experiments were carried out immediately after the prepolymer preparation process. Isothermal time sweep tests were performed with 25-mm disposable parallel plates under controlled displacement at a frequency of 1 Hz to monitor the viscoelastic properties of the epoxy resin as a function of the curing time. As an example, Figure 2 shows the viscoelastic properties of the 1:1 ECO/PA resin cured at 155°C. Note that the curing time (*x* axis) in Figure 2 was corrected with the prepolymer preparation time (~10 min) and the equilibration time in the rheometer (~3 min) before

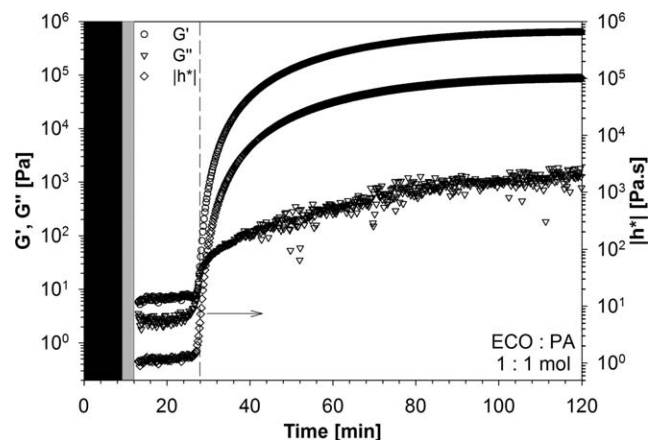


Figure 2. Viscoelastic properties of the ECO-based resin with an equimolar ratio of components cured at 155°C. The complex viscosity (η^*) of the resin. The vertical dashed line highlights the gelation time of the system. The black area corresponds to the prepolymer preparation time, and the gray area is the equilibration time in the rheometer.

isothermal curing; these times are shown in Figure 2 as dark and gray-filled areas, respectively. Also, the *y*-axis results are presented on logarithmic scales to allow the entire process to be presented.

As shown in Figure 2, during the initial period of curing, the sample behavior could be characterized as liquidlike. This region was characterized by low values of G' and G'' , and these values remained almost constant with time. Also, in this region, the mixture was in the sol state with a finite value of viscosity. Then, as the curing and, consequently, the crosslinking reaction progressed, the G' and G'' values of the system started to increase. At a certain point (~28 min for this particular system), the viscoelastic behavior of the system prevailed.³² This point, where a rapid increase of both the moduli and viscosity of the system were observed, was considered to be the gelation time for the system, as indicated by a dashed line in Figure 2.

It can be seen from the figure that as the gelation progressed, the viscosity of the system increased dramatically. In an ideal case, after gelation, the viscosity of the reactive mixture should tend toward infinite values. The observed finite values of the viscoelastic properties of this particular mixture within the experimental timeframe could be attributed to the structures, properties, and functionalities of the initial components of the resin. The structure of ECO (nonlinear chain, moderate MW) and the curing of ECO with aromatic acid anhydride (PA) led to the formation of flexible, rubberlike thermoset plastics, especially when they were synthesized at low a concentration of anhydride. In general, at low concentrations of curing agents, the molecular structure of the final resin likely consisted of a mixture of monomeric, oligomeric, and polymeric fractions, along with an unreacted epoxidized TAG. Excess epoxide simply became a diluent or plasticizer within the resin,³³ insoluble in the partially cured, hyperbranched, and crosslinked composition.³⁴ Hence, the ultimate MW of the heterogeneous resin depended on the initial concentration of the curing agent.³³ Hypothetically, a perfect thermoset network should have no free

components in the bulk, and the MW should be infinite.³⁵ However, too low of a concentration of curing agent will not allow the formation of single giant crosslinked macromolecule of resin because of the limited extent of reactions with the curing agent necessary to grow the macromolecule. Also, at a low curing agent content, the gelation of the system takes an extended period because of the low concentration of reactive groups. Because the final product is a flexible thermoset resin, the measurement of viscoelastic properties of the material was possible as a result of induced oscillation, even long after the established gelation period. At higher PA contents, the viscoelastic behavior of the system changed significantly. It can be seen from Figure 3 and Table II that for samples cured at the same temperature, an increase in the PA content accelerated the gelation process of the epoxy resin (lower values of gelation time), and the curing process was completed at a faster rate (increased slope under the linear part of the curve).

At low concentrations of PA and at low curing temperatures, the measurement of gelation times for the resins could be achieved, as described previously. However, at higher curing temperatures, the curing process started before the equilibrium temperature was achieved, and not surprisingly, this effect was also more pronounced for the resins with high PA contents. Thus, for the resins with a high PA content cured at high temperatures, the direct measurement of the gelation times was not possible, so an attempt was made to estimate these values by simple extrapolation.

In Table II, the values of the gelation times are highlighted in gray (italicized numbers) were those estimated from the extrapolation of the linear fitting of the experimental data. We observed that at lower curing temperatures (155 and 170°C), increasing the ECO/PA molar ratio from 1:1 to 1:2 decreased the gelation time by about a factor of 2.

However, at higher curing temperatures, the estimated gelation time became less dependent on the content of the curing agent.

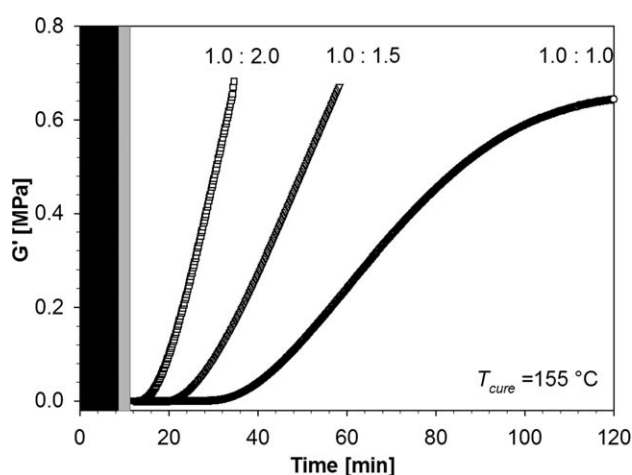


Figure 3. G' of the ECO and PA-based resin with different molar ratios of the components and with curing at 155°C as measured with a rheometer. The ratios of the components are indicated near the respective curves. The black area corresponds to the prepolymer preparation time, and the gray area is the equilibration time in the rheometer.

Table II. Gelation Time (min) of ECO/PA-Based Resins Cured at Different Temperatures as Determined from Rheological Experiments

ECO/PA (mol/mol)	T_{cure}			
	155°C	170°C	185°C	200°C
1.0:1.0	28	18	14	6
1.0:1.5	19	15	12	8
1.0:2.0	13	11	8	6

The italicized numbers were extrapolated from the linear trend. T_{cure} = curing temperature.

Similarly, increasing the curing temperature at a fixed concentration of PA led to faster curing rates and shorter gelation times. As an example of this, Figure 4 shows how G' of the 1:1 ECO/PA resin changed as a function of the curing time at different isothermal curing temperatures.

As shown in Figure 4, the resin cured at 155°C had an extended curing period. An increase in the curing temperature accelerated the reaction rate, and the viscoelastic properties of the cured resin reached their maximum value (under the conditions used) sooner at high temperatures.

In summary, both the temperature of curing and the concentration of curing agent were important variables in optimizing the formulation of the ECO/PA epoxy resins. There remains a need to establish which of these variables should best be manipulated to achieve the desired properties of the final product.

DMA

In general, epoxy resin formulations might exhibit enhanced or depressed mechanical properties, depending on the miscibility and reactivity of the components used. For anhydride-cured epoxy resins, it is expected that the anhydride molecules will directly participate in the curing reactions so that the anhydride residues will appear as part of the crosslinked structure of the final thermoset resin. Thus, in the ECO/PA system, the presence of anhydride (and an increase in its amount up to some limit)

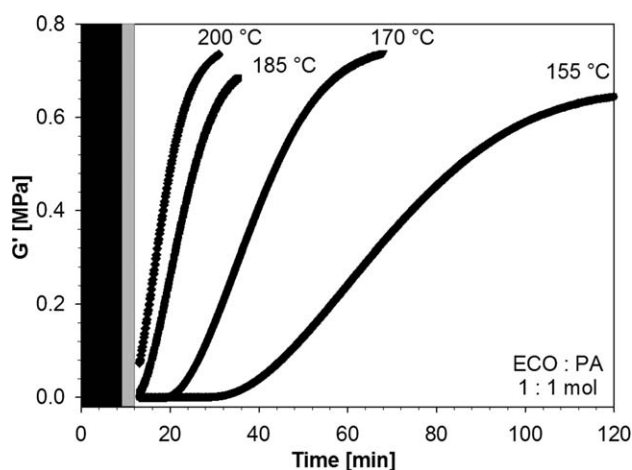


Figure 4. G' of the ECO and PA-based resin with an equimolar composition of the components at different temperatures as measured with a rheometer. The black area corresponds to the prepolymer preparation time, and the gray area is the equilibration time in the rheometer.

should have ultimately increased the formation of the cross-linked network structure of epoxy and, thus, reduced the polymer segment mobility and thereby increased the glass-transition temperature (T_g) of the material.

The DMA results in Figure 5 show the temperature dependence of G' and $\tan \delta$ for the ECO/PA resins prepared at different molar ratios and cured at a temperature of 155°C.

As shown in Figure 5, overall for all of the ECO/PA ratios, the dynamic mechanical behavior of the resins exhibited the typical, classic behavior of G' . Hence, the DMA plots showed a characteristic glassy plateau at very low temperatures and a dramatic decrease in the modulus above the T_g of the resin and reached a rubbery plateau. At low temperatures (below T_g), the resins showed that G' was inversely related to the PA content. For example, G' of the 1:1 ECO/PA resin was slightly higher at low temperatures than that of the other compositions.

It is well known that changes in the mechanical relaxation of polymer composites and blends can result from both changes in the molecular mobility of the matrix phase due to interactions at the polymer–filler or polymer–polymer interfaces and a mechanical coupling effect between phases.^{36,37} The transitions below T_g (so called sub- T_g transitions) are associated with the mechanical performance of materials in the glassy state. These transitions are described as being due to local motions, bond bending and stretching, and movements in the side chain or adjacent atoms in the main chain.³⁸ For instance, this transition has been attributed to the unreacted molecular segments and/or inhomogeneities in the epoxy samples arising from dissimilar crosslinked regions.³⁹ Thus, higher values of the modulus below the T_g s for the ECO/PA system with lower PA contents could have been due to the relaxation of the unbounded/unreacted epoxy monomer, depending on the concentration of the components. Similar behavior was also described for cured thermoset resins, where increased freedom of movement in the side chains increased the strength of the transition.³⁸ Thus, in this

case (Figure 5), an increase in the amount of curing agent led to enhanced crosslinking and a smaller quantity of free/side chains available for relaxation. Hence, the observed modulus at low temperatures was lower.

With increasing temperature, the large segments of the chain started to move, and the material transformed from a hard glass to a viscoelastic state at temperatures above the glass transition. The area above the T_g (and below the melting point, if it is a crystalline polymer) is known as the rubbery plateau, and the modulus in the plateau region depends on many factors, including the ratio of components, the chemical structure of the monomers, the number of crosslinks, and the chain length between entanglements.³⁸ In practice, the relative modulus of the plateau region gives an indication of the relative changes in the number of crosslinks in a material.⁴⁰ As shown in Figure 5, the resin cured with a low concentration of PA (1:1 mol/mol) exhibited a lower modulus in the rubbery plateau region compared to the resin with a high PA content because of the lower crosslink density. The equimolar system was also characterized by the lower values of T_g (see Table III) compared to the other compositions studied. The segmental mobility in the highly crosslinked resins were significantly hindered; hence, they exhibited a higher modulus in this region.

It was clear that in the rubbery plateau region, the dynamic mechanical properties were mainly determined by the segmental mobility of the crosslinked structures in the bulk resin, with the assumption that all of the PA reacted with ECO. This assumption was justified, as described earlier, because the PA molecule could potentially react with two epoxides, and each molecule of epoxidized oil had about four epoxide groups. Hence, even at a high content of PA (ECO/PA = 1:2), the expected stoichiometric ratio of reactive moieties of these components was close to 1:1, and the presence and contribution of unreacted PA to the mechanical performance was negligible. However, the presence of the higher number of PA units in the material may have also contributed to the modulus in the rubbery region because of some degree of change in the chemical structure within the material.

The temperature dependence of $\tan \delta$ of the resins with different ratios of the components are also plotted in Figure 5. This indicates similar trends to those discussed previously. As expected, the intensity of the $\tan \delta$ peak for equimolar ECO/PA was much higher than the peak of resins with higher amounts of PA. The intensity of the $\tan \delta$ peak was directly related to the initial ECO content in the system as the peak was associated with the relaxation of ECO units. The intensity of the $\tan \delta$ gradually decreased with increasing PA content. A significant decrease in the $\tan \delta$ peak intensity was observed in the resin with a high content of PA. This was expected because the formation of crosslinked structures restricted the molecular motions, and this caused the amount of energy that could dissipate throughout the bulk volume to decrease dramatically.¹⁷ This could have caused the T_g to shift to higher temperatures with increasing PA content, as shown in Figure 5.

The T_g is usually determined by the peak temperature of the dynamic G'' or by the temperature at which $\tan \delta$ exhibited the peak.^{37,41} Here, the T_g 's of the resins were measured from the

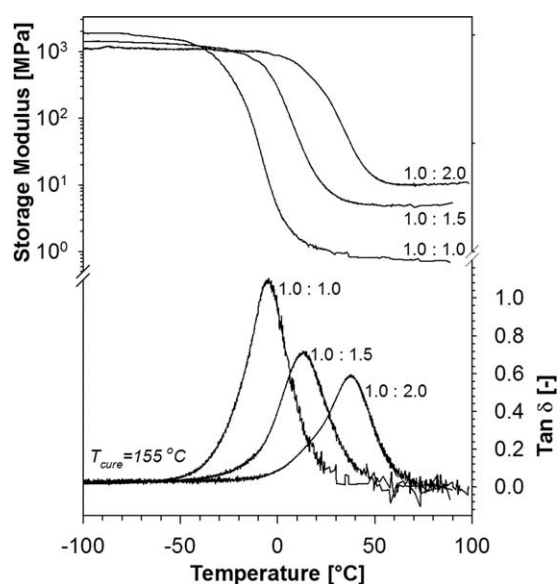


Figure 5. G' and $\tan \delta$ as functions of the temperature for the resin with different ratios of the components and with curing at 155°C.

Table III. T_g s (°C) of the ECO/PA-Based Resins Cured at Different Temperatures as Determined from DMA and Conventional DSC Experiments

ECO/PA (mol/mol)	T_{cure}							
	DMA ($\tan \delta$)				DSC			
	155°C	170°C	185°C	200°C	155°C	170°C	185°C	200°C
1.0:1.0	-3.6 ± 1.2	-4.4 ± 1.4	-4.4 ± 0.3	-3.3 ± 0.6	-24.1 ± 0.3	-25.2 ± 0.2	-24.4 ± 0.1	-23.9 ± 0.1
1.0:1.5	13.1 ± 0.4	13.5 ± 0.9	15.5 ± 1.1	17.7 ± 0.3	-16.8 ± 0.6	-17.2 ± 1.4	-12.4 ± 1.8	-10.3 ± 0.1
1.0:2.0	37.8 ± 0.6	40.4 ± 0.6	39.0 ± 0.1	39.1 ± 0.7	16.1 ± 1.0	16.8 ± 5.5	17.3 ± 1.1	18.2 ± 0.3

The uncertainties are standard deviations of at least duplicates.
 T_{cure} = curing temperature.

$\tan \delta$, that is, the peak of $\tan \delta$ (Table III). Although, DMA is believed more sensitive than DSC to measure the T_g of cross-linked thermoset materials,⁴² we also applied conventional DSC experiments (in modulation mode) to measure the T_g values of the cured materials (DSC traces are not presented here). The data presented in Table III indicates that the T_g of the resins varied little with the curing temperature, whereas an increase in the PA content significantly increased the T_g of the resin. The influence of the curing temperature and curing agent content on T_g is illustrated in Figure 6, which shows the T_g values determined by DMA.

It is shown in Figure 6(a) that the T_g 's of all of the systems studied were not dependent or were only weakly dependent on the curing temperature for the ECO/PA system over the temperature range studied. However, the influence of the content of the curing agent on the T_g of the final resin was significant [Figure 6(b)]. This strong dependence was observed as a linear regression plot of these data on the basis of the average values of T_g at a given composition.

Although, the values of T_g determined with DSC were significantly different from those determined by DMA, they followed exactly the same trends with the ECO/PA ratios and curing temperature. The observed difference in T_g measured by the

two techniques arose because of the different processes that DSC and DMA measure, as discussed in many previous works.^{43,44}

Thus, the T_g (and consequently, the mechanical properties) of the ECO/PA system largely depended on the amount of curing agent. Hence, we concluded that the curing process could be greatly accelerated by an increase in the curing temperature without a significant impact to the T_g . Alternatively, an improvement in the T_g of the material at a given temperature of curing could be achieved by the variation of the amount of curing agent.²⁹

CONCLUSIONS

A canola-oil-based epoxy resin was successfully produced and applied to the making of thermoset resins with PA as a curing agent. The curing process of the resin and the thermomechanical properties of the resin was characterized with different techniques.

The results show that careful selection of a combination of the curing temperature and ECO/PA ratio could be used to create a thermoset resin with preferred thermomechanical properties. For example, a thermoset resin with a particular modulus or T_g could be prepared at faster curing rate through the variation of the curing temperature alone. Alternatively, with fixed curing conditions, thermoset resins with diverse mechanical properties could be prepared by the variation of the amount of curing agent. The combination of these factors could be especially useful for the creation of composites with temperature-sensitive components, for example, lignocellulosic materials. In the manufacturing of these products (in these cases, there may be upper temperature limits to prevent the burning of lignocellulosic materials), the speed of curing and the final mechanical properties can be enhanced through an increase in the concentration of curing agent up to a certain amount. However, it should be noted that extreme curing rates may lead to structures with localized areas of high stress in the final resin, while excess amounts of curing agents, from the stoichiometric ratio of reactive groups, may lead to inhomogeneous structure formation. Such inhomogeneities may significantly affect the impact properties of the materials. An important finding during our resin preparation was that the oligomeric prepolymers of ECO and PA were relatively stable under ambient conditions and when they had been stored for several days without curing. The resins

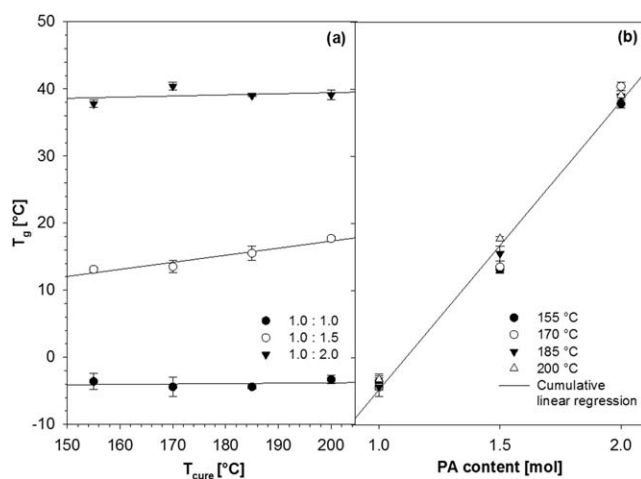


Figure 6. (a) Temperature and (b) concentration dependence of the T_g for ECO/PA resins. The error bars are the standard deviations of at least duplicates. The cumulative linear regression was plotted with the average values of T_g for the respective compositions.

reported here could also be used as aldehyde-free alternatives for aldehyde-containing internal bonding adhesives (melamine, urea, or phenol formaldehyde) to manufacture lignocellulosic fiberboard or particleboard. We demonstrated the applicability of this resin in the making of lignocellulosic fiber- and particle-based biocomposites (not reported here) with a diversity of cellulosic fibers, fiber mats, and forestry wastes. The increased diversity in the properties of similar resins could be achieved with other unsaturated plant and animal oils and result from a change in functionality. Thus, changing the type and functionality of the curing agent or the functionality of the epoxy precursor adds another important variable. For example, the curing process could be completed at faster rates with highly functional epoxidized linseed oil (with an average of 6.5 epoxy groups per TAG) compared to the moderately functional ECO (with 3.9 epoxy groups per epoxidized TAG).

In summary, thermoset resins with a range of predesigned thermomechanical properties and reactivities may be produced by the careful selection of the curing conditions and biobased oil epoxide reactants.

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