Synthesis and properties of cross-linked polymers from epoxidized rubber seed oil and triethylenetetramine

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ABSTRACT: A series of epoxidized oils were prepared from rubber seed, soybean, jatropha, palm, and coconut oils. The epoxy content varied from 0.03 to 7.4 wt %, in accordance with the degree of unsaturation of the oils (lowest for coconut, highest for rubber seed oil). Bulk polymerization/curing of the epoxidized oils with triethylenetetramine (in the absence of a catalyst) was carried out in a batch setup (1 : 1 molar ratio of epoxide to primary amine groups, 100°C, 100 rpm, 30 min) followed by casting of the mixture in a steel mold (180°C, 200 bar, 21 h) and this resulted in cross-linked resins. The effect of relevant pressing conditions such as time, temperature, pressure, and molar ratio of the epoxide and primary amine groups was investigated and modeled using multivariable nonlinear regression. Good agreement between experimental data and model were obtained. The rubber seed oil-derived polymer has a T_g of 11.1°C, a tensile strength of 1.72 MPa, and strain at break of 182%. These values are slightly higher than for commercial epoxidized soybean oil (T_g of 6.9°C, tensile strength of 1.11 MPa, and strain at break of 145.7%). However, the comparison highlights the potential for these novel resins to be used at industrial/commercial level. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42591.

INTRODUCTION

Epoxy resins are widely used as structural adhesives due to their superior mechanical properties, chemical resistance, and high temperature service capability.[1] The glass transition temperature (T_g) is one of the most important product property of an epoxy resin as it determines the window of applications. High T_g (100–150°C) resins are typically required for structural adhesives and sheet molding compound,[2,3] whereas low T_g ones (<30°C) are suitable as adhesives for electronic and automotive applications.[4] The global market for epoxy resins is estimated to reach 8.7 billion USD by 2017.[5] Currently, most epoxy resins are made from fossil resources.

Plant oils have received considerable attention as renewable resources for the production of energy and chemicals in general and as a starting material for polymers with product properties in the range for commercial epoxy resins in particular.[6] Epoxidized plant oils are attractive starting materials for such advanced materials and are already available on industrial scales and widely used as plasticizers and stabilizers for the production of polyvinyl chloride (PVC).[7–9] Epoxidized soybean and linseed oils are particularly attractive due to their high reactivity associated with the high content of unsaturated fatty acids. The high reactivity of the epoxide group offers the possibility to perform curing reactions, e.g., with multifunctional amines.[10] For instance, epoxidized soybean oil has been used for the synthesis of new bio-based thermosetting resins and also as a toughening agent in epoxy resins.[1,11]

A potentially very attractive plant oil for the synthesis of advanced materials is the oil from rubber seeds of the rubber tree (*Hevea brasiliensis*). So far, the tree has been cultivated mainly as an industrial crop for the production of natural rubber and valorization of the seeds has received limited attention. Rubber seed oil (RSO) is particularly attractive as it has a relatively high content of unsaturated fatty acids.[12,13] In this article, we report our findings on the epoxidation of RSO oil and the subsequent application of the epoxidized rubber seed oil as a starting material for the synthesis of novel resins.

Numerous studies have been carried out on the epoxidation of plant oils using organic peracids such as performic acid, generated *in situ* using hydrogen peroxide.[14–19] The epoxidation of RSO using performic and peroxyacetic acid generated *in situ* has been reported in the literature.[13,20] It is possible to achieve
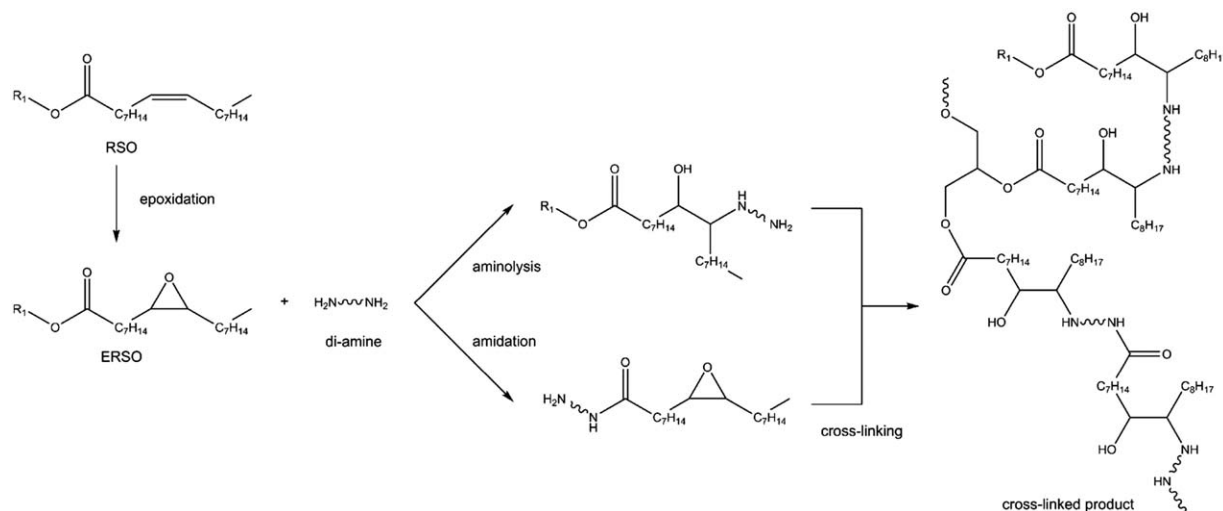
Figure 1. Reaction pathway for the cross-linking of ERSO with amines (RSO is represented by oleic acid and R_1 is the remaining triglyceride structure consisting of different saturated and unsaturated fatty acids).

up to 91% olefin conversion to epoxides after 5 h reaction time at 60°C (molar ratio carbon–carbon double bonds to HCOOH to H_2O_2 of 2 : 1 : 4).[20]

Several studies on the utilization of epoxidized RSO (ERSO) as plasticizer and stabilizers on PVC have also been reported.[21,22] However, cross-linking/curing of ERSO with a multifunctional amine compounds (in analogy to the curing chemistry of commercial epoxy resins) for the preparation of the corresponding resins has, to the best of our knowledge, not been reported. In this article, a systematic study on the cross-linking of ERSO with triethylenetetramine (TETA) to develop novel resins is reported. The reaction envisaged chemistry for the cross-linking of ERSO with the amine is illustrated in Figure 1.

The first part describes the synthesis of cross-linked polymers from a series of epoxidized oils (EO, being RSO, soybean oil (SO), jatropha oil (JO), palm oil (PO), and coconut oil (CO). Bulk polymerization/curing of the epoxidized oils with triethylenetetraamine (without the use of a catalyst) was carried out in a batch setup (1 : 1 molar ratio of epoxide to amine primary groups, 100°C, 100 rpm, 30 min) followed by casting of the mixture in a steel mold (180°C, 200 bar, 21 h) resulted in cross-linked resins.

The second part describes an experimental study to correlate process conditions, particularly temperature, pressure, molar intake of the epoxy to amine groups, and pressing time with relevant product properties like thermal behavior (T_g and onset decomposition temperature, T_{onset}). A total of 40 experiments were performed. The T_g and T_{onset} of the resulting product were modeled using multivariable nonlinear regression. Such quantitative data are not yet available for the cross-linking of ERSO with amines. The optimum conditions (in terms of T_g and T_{onset}) for the cross-linking of ERSO with TETA were also applied to prepare a range of resins from other epoxidized plant oils (SO, JO, PO, CO) with the objective to determine epoxide structure–resin property relations.

EXPERIMENTAL

Materials

The RSO oil was obtained by pressing rubber seeds from Bengkulu, Indonesia using a standard hydraulic press. Soybean and coconut oil were purchased from Albert-Heijn and Deli-XL, the Netherlands, respectively. Palm oil was obtained from IOI Loders Croklaan, the Netherlands and jatropha oil form Diligent, the Netherlands. Hydrogen peroxide (30 wt %, pro analysis), triethylenetetramine (97%), epoxidized soya bean oil (analytical standard) and $CDCl_3$ (99.8%) were obtained from Sigma Aldrich. Toluene (99.5%) was obtained from Lab Scan whereas formic acid (ACS reagent, 99%) was obtained from Merck Chemicals.

Experimental Procedure for the Epoxidation of Plant Oils

The plant oil was mixed with toluene and formic acid (1 : 12 : 4 mol ratio with respect to the carbon–carbon double bond of the plant oil) in a three necked round bottom flask (500 mL) equipped with a water bath, a magnetic stirrer, a condenser, and a dropping funnel. H_2O_2 (1 : 25 mol ratio with respect to the carbon–carbon double bond of the plant oil) was added dropwise while stirring at 400 rpm and 60°C for 0.5 h and the reaction mixture was stirred for another 1–12 h. After reaction, the water and toluene layer were separated. The toluene phase with the EO was washed with a brine solution (5 wt % NaCl) until no peroxide was left in the mixture (peroxide test paper as an indicator). The toluene was removed by evaporation (55°C, 100 mbar) followed by drying in a vacuum oven (55°C, 100 mbar) till constant weight (up to 48 h). The EO was analyzed by ^{1}H-NMR and FT-IR. The epoxide conversion for RSO, JO, SO, and PO is approximately 97 mol %, whereas the conversion for CO is around 58 mol %.

Preliminary Experiments on the Amidation of Oil with TETA

The plant oil (RSO, SO, JO, PO, and CO) was mixed with TETA using a 1 : 1 molar ratio of carbon–carbon double bonds to primary amine groups and mixed at three different

temperatures, i) viz. 20°C for 15 h, 100°C for 0.5 h, and 150°C for to 2 h. The resulting products were analyzed using ^{1}H-NMR and FT-IR.

Cross-Linking of EO with TETA

The EO was mixed with TETA at different molar ratios of the epoxide and primary amine groups (0.25–2). The mixture was heated at 100°C and stirred at 100 rpm for 30 min. Afterward, the mixture was poured into a steel mold plate (100 × 100 × 1 mm^3) and pressed at 100–200 bar and 100–200°C (Schwaben-than Polystat 100T) at different pressing times (6–48 h).

Statistical Modeling and Optimization

Nonlinear multivariable regression was used to model the experimental date and for this purpose the Design Expert Version 7.0.0 software package was used. The following equation was used:

$$y = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{4} b_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} b_{ij} x_{ij} + e \qquad (1)$$

Where y is the dependent variables (T_g and T_{onset}), x_i and x_j are the independent variables (molar ratio of epoxide to primary amine groups, pressing time, temperature, and pressure), b_o, b_i, b_{ii}, and b_{ij} are the regression coefficients of the model, whereas e is the error of the model.

The regression equations were obtained by backward elimination of statistically nonsignificant parameters. A parameter was considered statistically relevant when the P value was less than 0.05. The best conditions to obtain products with the highest T_g were obtained using the numerical optimization function provided in the software package.

Product Analysis

The carbon–carbon double bond conversion in the plant oil epoxidation reaction was determined using ^{1}H-NMR. A few drops of the EO were added to CDCl$_3$ and then analyzed using a 200 MHz Varian NMR. The conversion was determined by comparing the intensity of the characteristic quartet signal of the remaining carbon–carbon double bond in the epoxidized oil (δ 5.23 ppm) with respect to the signal of the methyl end group of the fatty acids (δ 0.9 ppm) divided by the intensity of the characteristic quartet signal of the initial carbon–carbon double bond in the oil (δ 5.23 ppm) with respect to the signal of the methyl end group of the fatty acid chain (δ 0.9 ppm).

$$\text{Epoxide conversion} = 1 - \frac{\left(\frac{DB}{ME}\right)_{EO}}{\left(\frac{DB}{ME}\right)_{oil}} \times 100\% \qquad (\text{mol}\%) \qquad (2)$$

Where,

DB   carbon–carbon double bond peak area

ME   methyl end group peak area

^{1}H-NMR of EO (200 MHz, CDCl$_3$) δ_H (ppm): 0.83–0.89 (C$\textbf{\textit{H}}_3$CH$_2$), 1.22-1.58 (—C$\textbf{\textit{H}}_2$—), 1.68–1.73 (—CHOCHC$\textbf{\textit{H}}_2$CHOCH—), 2.26–2.31 (—C$\textbf{\textit{H}}_2$COO—), 2.86–3.09 (—C$\textbf{\textit{H}}$OHC$\textbf{\textit{H}}$—, epoxide), 4.09–4.28 (OCH(C$\textbf{\textit{H}}_2$)$_2$), 5.23 (OC$\textbf{\textit{H}}$(CH$_2$)$_2$).

The epoxy oxygen content (EOC) was determined with a nonaqueous titration method as proposed in the literature.[23] The sample (0.5 g) was dissolved in 10 mL acetone and 10 mL of hydrobromic acid (0.1 M in acetic acid). A few drops of crystal violet

indicator were added and the solution was titrated with perchloric acid (0.1 N) until a sharp visual end point was obtained.

The fatty acid composition of the oil was analyzed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 series II Plus device. A detailed description of the GC method is described elsewhere.[24]

The acid value of the sample was measured by an acid–base titration using phenolphthalein as the indicator. A detailed description of the method is described elsewhere.[24]

The iodine value of the oil can be estimated from the number of carbon–carbon double bonds per triglyceride molecule as shown in Eq. (3).[25]

$$\text{Iodine value} = 100 \times \frac{MW_{I_2} \times db}{MW_{oil}} \qquad (\text{mg } I_2/\text{g}) \qquad (3)$$

Where,

db average number of carbon–carbon double bonds per triglyceride molecule

MW$_{I2}$ molecular weight of iodine (g/mol)

MW$_{oil}$ molecular weight of oil (g/mol).

The viscosity of a product sample was determined using a rheometer AR1000-N from TA instrument. A cone-and-plate viscometer was used with a cone diameter of 40 mm and a 2° angle. The measurement was performed at 40°C with a shear rate of 15 s^{-1}.[26]

The C and H content of the samples were determined by the elemental analyses on an automated Euro EA3000 CHNS analyzer with acetanilide as a calibration reference. All samples were analyzed in duplicate and the average value is reported.

FT-IR spectra were recorded on a Bruker IFS88 spectrometer equipped with golden gate MCT-A detector.

Differential scanning calorimetry (DSC) analysis was performed using a DSC 2920 from TA instrument with a heating rate of 10°C/min and cooling rate of 10°C/min. The glass transition temperature, T_g was determined from the inflection point of the second scanning curve.

Tensile properties were measured using an Instrom 5565 instrument using the ASTM D638 standard. Dumbell-shaped samples obtained from the molded resin sheets were used. The samples were measured in triplicate and average values are reported.

Dynamic mechanical thermal analyses (DMTA) were carried out using a rheometrics scientific solid analyzer (RSA II). The testing was performed in a tension mode with a strain of 0.5% and a mechanical vibration frequency of 1 Hz at 20°C.[27]

Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA 7. Samples were heated at a heating ramp of 10°C/min under nitrogen. The definition of the T_{onset} is provided in Figure 2.[2]

RESULTS AND DISCUSSION

Synthesis and Properties of Epoxidized Oils (EO)

The epoxidation of five oils with different amounts of carbon–carbon double bonds was investigated, *viz.*, RSO, SO, JO, PO,
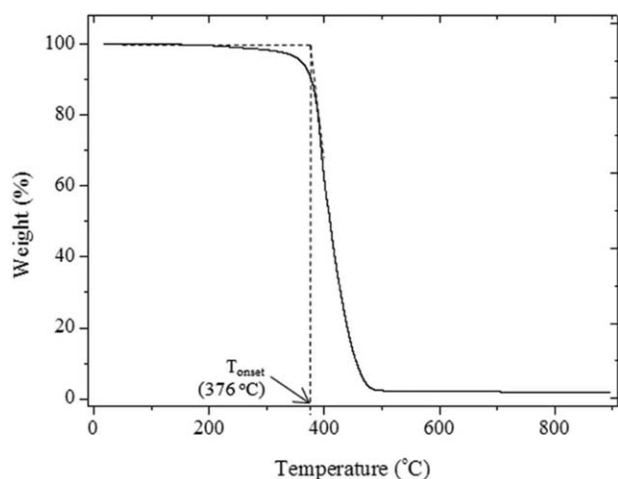
Figure 2. TGA profile for a representative sample showing the determination of the T_{onset}.

and CO. The fatty acid composition of the oils was determined (GC) and the results are shown in Table I.

RSO, SO, and JO have a high content of unsaturated fatty acid chains, whereas PO and CO are more saturated. The average number of carbon–carbon double bonds per triglyceride molecule was also determined (^{1}H-NMR) and the results are presented in Table I. RSO and SO have the highest amount of carbon–carbon double bond per triglyceride molecule (4.7 and 4.6, respectively) followed by JO (3.7), PO (1.9), and CO (0.4), in line with the fatty acid composition as determined by GC. The theoretical iodine value (IV) of the oils was estimated from the number of carbon–carbon double bonds per triglyceride and is shown in Table I. The iodine values are within the range reported in the literature for RSO (120–136 mg I$_2$/g), SO

(120–136 mg I$_2$/g), and JO (91–113 mg I$_2$/g). The iodine values for PO (44–58 mg I$_2$/g) and CO (7–10 mg I$_2$/g) are slightly higher than for the range reported in the literature.[29–32] A possible explanation is that the average number of carbon–carbon double bonds per triglyceride molecule as estimated from the ^{1}H-NMR spectra for PO and CO is slightly over estimated due to inaccuracies in the integration data. The acid values for SO, PO, and CO (0.1–0.9 mg KOH/g) are relatively low. Higher values are found for RSO (14.1 mg KOH/g oil) and JO (8.9 mg KOH/g oil), which may affect the reactivity in the subsequent curing chemistry. All oils were used for the epoxidation experiments without further purification.

Preliminary epoxidation experiments with RSO were carried out in a batch setup using a carbon–carbon double bonds to formic acid to hydrogen peroxide molar ratio of 1 : 4 : 25 at 60°C.[28] The batch time was varied from 1–12 h to determine the carbon–carbon double bond conversion as a function of the batch time (^{1}H-NMR).

Figure 3 shows that the carbon–carbon double bonds conversion reached a maximum value of 97 mol % after approximately 6 h reaction time. The number of epoxide groups in the product oils, as measured by the epoxy oxygen content (EOC), increased also with time before it reached a maximum of 7.4 wt % after approximately 6 h. Hence, a reaction time of 6 h is sufficient for a maximum conversion of the carbon–carbon double bonds.

Based on the preliminary experiments with RSO, the epoxidation of the other oils was carried out at similar conditions (1 : 4 : 25 molar ratio of carbon–carbon double bonds: formic acid: hydrogen peroxide, 60°C, 400 rpm) for 12 h to ensure maximum conversion of the carbon–carbon double bond and highest EOC values. Approximately 97 mol % conversion was achieved for SO, JO and PO. However for CO, only 58 mol % conversion was obtained, even after the experiment was extended for 24 h. Thus, the epoxidation reaction is far from
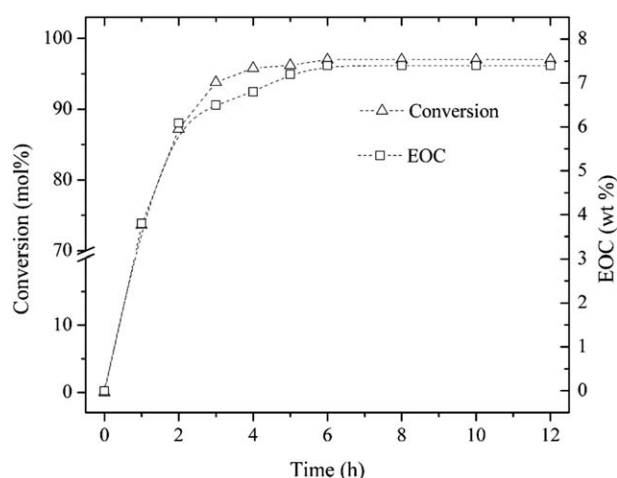
Table I. Relevant Properties and Fatty Acid Composition of the Various Oils Used in this Study

	RSO	SO	JO	PO	CO
Capric acid (C$_{10:0}$)					5.6
Lauric acid (C$_{12:0}$)		0.3			54.9
Myristic acid (C$_{14:0}$)		1.0		1.7	21.6
Palmitic acid (C$_{16:0}$)	8.2	10.3	15.1	36.5	9.5
Stearic acid (C$_{18:0}$)	7.3	3.4	5.3	3.3	2.3
Oleic acid (C$_{18:1}$)	28.1	27.6	41.9	49.3	4.4
Linoleic acid (C$_{18:2}$)	38.2	52.0	37.7	9.2	1.7
Linolenic acid (C$_{18:3}$)	14.2	5.4			
Carbon–carbon double bond[a]	4.7	4.6	3.7	1.9	0.4
Iodine value (mg I$_2$/g)[b]	134.4	133.9	108.2	58.5	14.9
Acid value (mg KOH/g)	14.1	0.3	8.9	0.9	0.2

[a] Average number of carbon–carbon double bonds per triglyceride.
[b] Theoretical iodine value estimated from the number of carbon–carbon double bonds per triglyceride.

Figure 3. Carbon–carbon double bond conversion (mol %) of RSO and the number of epoxide groups in the product oils Expressed as the epoxy oxygen content (EOC, wt %) versus time (1 : 4 : 25 molar ratio of carbon–carbon double bonds: formic acid: hydrogen peroxide, 60°C, 400 rpm).

Table II. Composition and Product Properties of EOs[a]

EO	Elemental analysis			EOC (wt %)	Viscosity (Pa s)	Acid value (mg KOH/g)
	O (wt %)[b]	C (wt %)	H (wt %)			
ERSO	18.1	71.3	10.6	7.4	0.20	9.0
ESO	17.5	71.8	10.7	6.5	0.17	0.2
EJO	16.3	72.7	11	5.9	0.23	7.8
EPO	15.1	73.4	11.5	0.7	0.09	0.3
ECO	14.6	73.8	11.6	0.03	0.04	0.1

[a] N content in all samples below 0.01 wt %.
[b] By difference.

quantitative for CO, likely due to a lower degree of unsaturation for this particular oil.

Product Properties of the EOs

Relevant product properties of the EOs are presented in Table II. The EOC values are within the range reported in the literature for ESO (6.5–6.9 wt %), EJO (5.1–6.1%), and EPO (0.3–2.5 wt %).[33–36] The oxygen content of the products as determined by elemental analysis is highest for ERSO (18.1 wt %), followed by ESO (17.5 wt %), EJO (16.3 wt %), EPO (15.1 wt %), and ECO (14.6 wt %). The EOC values and the oxygen content nicely correlate, higher EOC values and thus a higher amount of epoxide groups per triglyceride leads to higher oxygen content of the product.

The viscosity of the EOs is in the range of 0.04–0.23 Pa s, with the lowest values for EPO and ECO. It is well known that the viscosity of epoxidized oils is higher than that of the parent oil.[16] For instance, the viscosity of EJO (0.23 Pa s) is about one order of magnitude higher than the viscosity of JO as previously reported in our group (0.034 Pa s).[37] As such, a low viscosity should correspond with a low amount of epoxide groups and this is indeed the case.

The acid value of the EOs is in the range of 0.1–9 mg KOH/g and the highest values were found for ERSO and EJO. This is due to the higher acid value of the starting materials. However,

the acid value of the EOs is lower than the one of the corresponding oils (Table I), indicating that ester hydrolysis is negligible during the epoxidation reaction.

The FT-IR spectra of the EOs are provided in Figure 4. Epoxide peaks at around 820 and 840 cm^{-1} are particularly visible for the EO's with the highest amount of epoxide groups (ERSO, ESO, and EJO). The absence of OH band in the FT-IR spectra (Figure 4) indicates that ring opening of the epoxide to the corresponding vicinal diols does not occur to a significant extent.[16]

Synthesis of Cross-Linked Polymers

Epoxidized plant oils not only contain reactive epoxide groups but also ester groups which may also show reactivity with amines and form amides. Hence, simultaneous aminolysis of the epoxy group and amidation of the ester group may take place during the cross-linking with amines as shown in Figure 1. The latter is normally not taken into account because amidation does not hinder network formation.[14] However, amidation reduces the average number of reactive epoxy groups per triglyceride molecule. This may affect the structure and properties of the cross-linked polymers and contribute to the formation of "structurally looser" networks.

Preliminary Experiments on the Reactivity of TETA and Plant Oils

To gain insight in the rate and extent of the amidation of ester groups with amines, a number of reactions were carried out with the plant oil feed and TETA. The plant oil was mixed with TETA at 1 : 1 molar ratio of carbon–carbon double bond to primary amine groups. Figure 5 the shows typical ^{1}H-NMR spectra of RSO mixed with TETA at different temperatures and mixing/heating times. At prolonged batch times, new signals appeared at δ 3.19–3.80 ppm which indicates the formation of amide groups —C(=O)—NH—CH$_2$ groups.[14] In TETA, the NH—CH$_2$ resonances are present at δ 2.89 ppm. The intensity of the resonances between δ 4.09 and 4.28 ppm, originating from the —CH$_2$ group of the triglyceride backbone, decreased with time. Proton signals of the hydrogens attached to the α-carbon of the carboxyl group (—O—(O=C)—CH$_2$) shifted from δ 2.3 ppm to δ 2.10. This indicates the occurrence of an amidation reaction, as previously observed for the amidation of SO with n-hexylamine.[14] From Figure 5, it can be observed that amidation took place even at room temperature though is more pronounced at higher temperatures and longer mixing and/or heating times. Similar ^{1}H-NMR spectra were also observed for
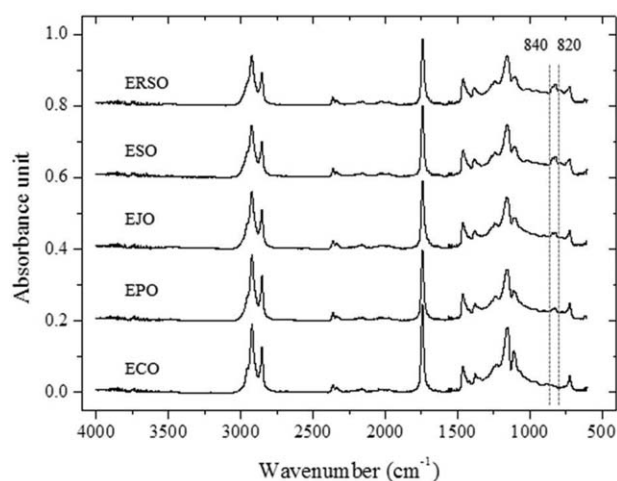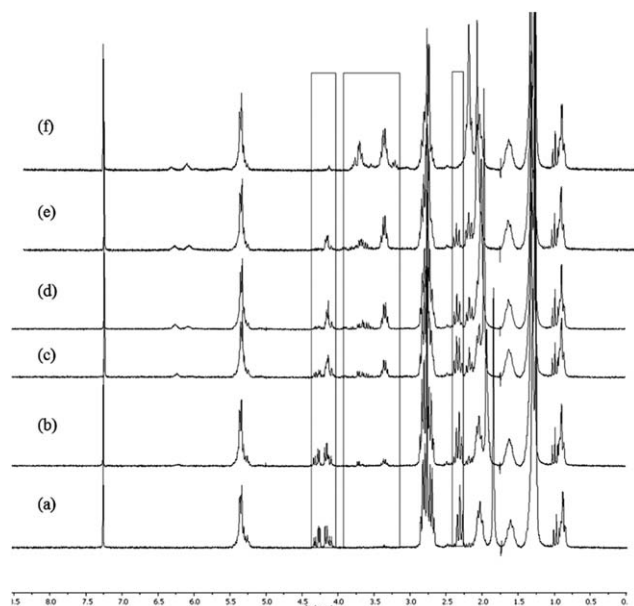

Figure 4. FT-IR spectra of epoxidized EOS.

Figure 5. Typical ^{1}H-NMR spectra (CDCl$_3$) of RSO mixed with TETA: (a) 20°C, 0 h, (b) 20°C, 2 h, (c) 20°C, 5 h, (d) 20°C, 15 h, (e) 100°C, 0.5 h, and (f) 150°C, 2 h.

the reactions of the other vegetable oils with TETA (data not shown for brevity) indicating that (partial) amidation also occurred for the other oils.

The conversion of the ester group can be estimated from ^{13}C-NMR studies. At the most severe conditions (150°C, 2 h), the conversion of the ester group to the amide is quantitative (almost 100% conversion). This is evident from the disappearance of the resonances from the ester carbons (—OO**C**—CH, δ 172.9 and 173.4 ppm) as shown in Figure 6. A new signal appeared at δ 173.7 ppm which indicates the presence of an amide group, in line with the ^{1}H-NMR data.

The FT-IR spectra as shown in Figure 7 also confirm the formation of an amide unit and characteristic peaks of the amide are present at 1635 and 1560 cm^{-1}. In line with the occurrence of an amidation reaction is a reduction of the intensity of the ester group (1735 cm^{-1}) upon reaction with TETA.
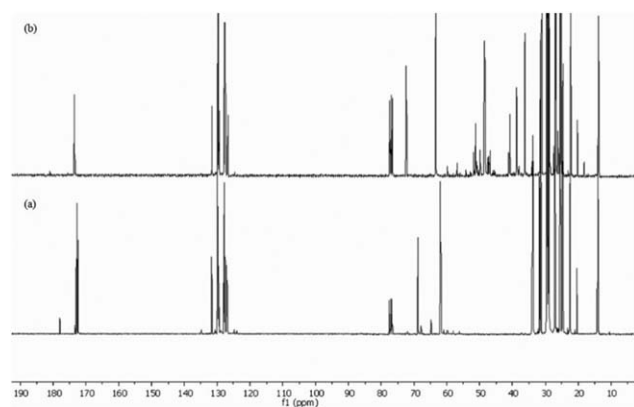

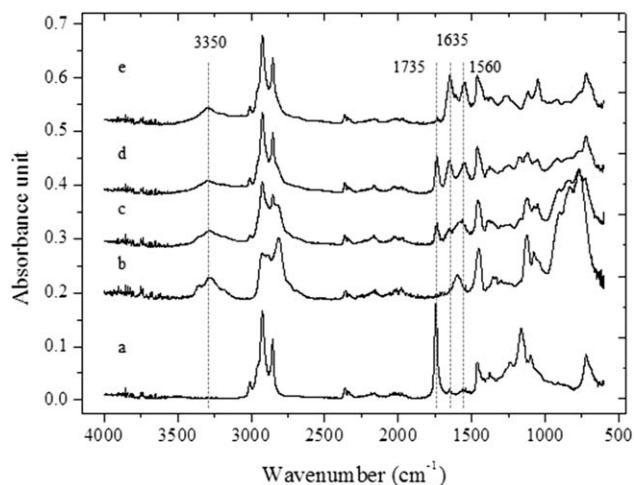**Figure 6.** Typical ^{13}C-NMR spectra (CDCl$_3$) of (a) RSO and (b) RSO mixed with TETA (150°C, 2h).

Figure 7. The FT-IR spectra for RSO (a), TETA (b) and RSO mixed with TETA at (c) 20°C, 0.5 h (d) 100°C, 0.5 h (e) 150°C, 2 h.

Thus, we can conclude that ester amidation is an important reaction to be considered during the cross-linking of EOs with TETA, a fact often neglected in the literature on this subject. At higher temperatures and longer mixing and/or heating times, the extent of amidation increases and as such may affect the rate of the aminolysis reaction. However, the actual extent of the amidation reaction will depend on the relative rate differences between the two competitive amidation and the aminolysis reaction. Amidation may be of less importance when the aminolysis reaction is much faster than the amidation reaction.

Screening Experiments for the Cross-Linking of EOs with TETA

The cross-linking experiments of EOs (ERSO, ESO, EJO, EPO, and ECO) with TETA were carried a batch setup followed by casting of the mixture in a steel mold. Initial screening experiments were carried out at conditions close to those previously used in our group for the cross-linking of EJO with TETA[28] and involves an initial reaction/pre-mixing in a batch setup (variable molar ratio of epoxide to primary amine groups, 100°C, 100 rpm, 30 min) followed by casting of the mixture in a steel mold at different process conditions (Table III).

Typical FT-IR spectra of the cross-linked polymers are shown in Figures 8 and 9 and indicate that both aminolysis and amidation occurred during the cross-linking reaction. The C=O vibration at 1735 cm^{-1}, arising from the ester bonds, decreases

Table III. Overview of Experimental Conditions for the Synthesis of Cross-Linked Polymers from EOs and TETA

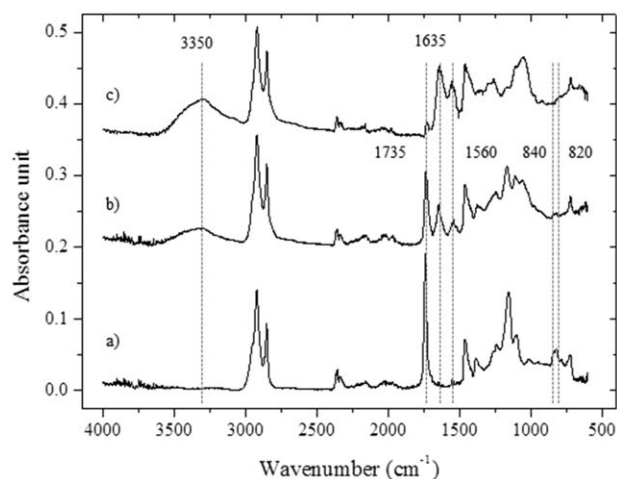| Variable	Screening	Systematic study
Mold temperature, T (°C)	150	100–200
Mold pressure, P (bar)	150	100–200
Pressing time, t (h)	15	6–48
Molar ratio of epoxy to primary amine groups (-)	1	0.25–2

Figure 8. FT-IR spectra of (a) ERSO and (b) PERSO just after mixing with TETA, and (c) after cross-linked with TETA (cross-linking conditions: 150°C, 150 bar, 15 h, 1 : 1 molar ratio of epoxy to primary amine group).

in intensity while two amide vibration bands at 1635 (C=O) and 1560 cm^{-1} (N=H) appear for all cross-linked polymers. In addition, a strong sharp signal around 3350 cm^{-1} (N=H), absent in TETA (Figure 7), confirms the presence of secondary amide, formed by the amidation of the EOs with TETA.

The T_g of the cross-linked polymers was determined by DSC, the resulting values ranging from −3.5 to 6.2°C. ERSO-based polymer (PERSO) had the highest T_g (6.2°C) followed by ESO-based polymer (PESO, 4.4°C) and EJO-based polymer (PEJO, 2.7°C). Palm oil-based polymer (PEPO) had the lowest T_g (−3.5°C), whereas the product of coconut oil based polymer (PECO) had no detectable T_g as measured by the DSC. In comparison to other cured resins, PERSO has the highest T_g. Hence, a systematic study was performed to optimize the cross-linking of ERSO with TETA in a laboratory scale pressing machine with the objective to obtain a high T_g and T_{onset}.

Systematic Studies on the Cross-Linking of ERSO with TETA
Systematic studies were carried out to investigate the effect of process conditions and particularly the temperature, pressure, time and molar ratio of epoxy to primary amine group on the T_g and T_{onset} of the cross-linked polymers. From the screening reactions for the cross-linking of EOs with TETA, the pre-heating of ERSO mixture with TETA was performed at 100°C for 0.5 h. An overview of the ranges of process variables for the systematic study is given in Table III. One of the experiments was carried out six times to determine the reproducibility of the experimental set-up. The relative error (based on the standard deviation) on the T_g and T_{onset} was 1.8% and 3.2%, respectively.

The results for all experiments are given in Table IV. The T_g ranged between −24 and 12.9°C, whereas the T_{onset} between 321 and 365°C. The highest T_g (12.9°C) and T_{onset} (365°C) within the experimental window were obtained at 1 : 1 molar ratio of epoxy to primary amine groups, pressing temperature and pressure of 200°C and 200 bar, respectively, with a pressing

time of 24 h. A tensile test was performed to determine the mechanical properties of some representative polymers, *viz.* from run 3 (T_g: 6.9°C), Run 23 (T_g: 4.8°C), and Run 28 (T_g: 12.9°C) and the results are shown in Table V and Figure 10.

From Figure 10, it can be observed that the tensile strength increased from 0.56 (Run 23) to 1.77 MPa (Run 28) as the T_g increased from 4.8 (Run 23) to 12.9°C (Run 28). The increase in T_g may be contributed by the increase in cross-link density and consequently lead to high modulus and strength.[27] An increase in T_g and modulus normally results in a high stiffness, which is normally accompanied by a low percentage of strain at break.[27] However, we observed otherwise, likely because the cross-linked polymers prepared in this study are in the "leathery"[27] state ($T_g \pm 10$°C), which results in a higher strength than rubbery materials and allows for higher elongations.

Regression Model for T_g
The experimental data given in Table IV were used as input for the development of multivariable nonlinear regression model for the T_g as a function of process conditions The coefficients for the regression model for the T_g are provided in Table VI and relevant statistical data are given in Table VII. The p-value of the model is very low ($<10^{-4}$) which indicates that the model is statistically significant. The parity plot (Figure 11) shows that the model fits the experimental data reasonably well. The effects of the process variables on the T_g are provided in three-dimensional response surface plots provided in Figure 12. The model predicts the existence of an optimum T_g value within the process window [Figure 12(b–d)].

Increasing the pressing time from 6 to 24 h increases the T_g, which indicates that network formation still occurs after 6 h reaction time. However, a further increase in the pressing time up to 48 h results in a lowering of the T_g. This is most likely due to thermal degradation as previously observed by our group for the pressing of cross-linked EJO with amine.[28] Increasing
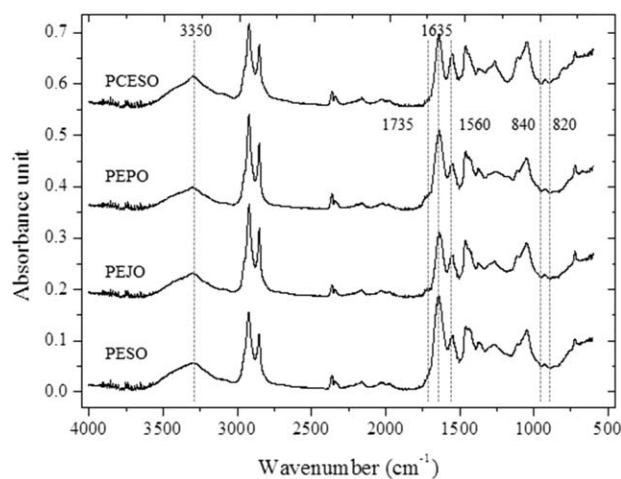

Figure 9. FT-IR spectra of polymers derived from the cross-linking of EOs with TETA (150°C, 150 bar, 15 h, 1 : 1 molar ratio of epoxy to primary amine group).

Table IV. Overview of Experimental and Modeled T_g and T_{onset} for the Cross-Linked Polymers

Run	T (°C)	P (bar)	t (h)	R (−)	T_g (°C)		T_{onset} (°C)	
					Data	Model	Data	Model
1	200	200	6	0.5	1.7	4.1	345.0	345.4
2	150	150	6	0.75	1.2	2.4	348.0	344.8
3	150	150	15	0.75	6.9	6.0	349.3	350.8
4	150	150	15	0.75	8.4	6.0	351.2	350.8
5	150	150	15	0.75	4.1	6.0	345.8	350.8
6	200	100	6	0.5	2.5	0.7	340.0	340.1
7	100	200	6	1	−5.9	−10.2	342.8	340.1
8	200	150	15	0.75	6.1	8.5	351.6	355.0
9	150	150	15	1	6.2	7.3	355.7	353.3
10	100	100	6	1	−17.2	−13.5	330.3	334.7
11	100	100	6	0.5	−21.2	−19.9	323.4	323.7
12	150	200	15	0.75	7.8	7.7	351.6	353.4
13	150	150	24	0.75	7.2	6.3	355.5	350.9
14	150	150	15	0.5	4.3	2.6	345.1	345.9
15	100	150	15	0.75	−10.9	−10.4	336.5	335.8
16	150	100	15	0.75	3.5	4.3	344.5	348.1
17	100	100	24	1	−6.7	−9.6	335.9	334.4
18	100	200	6	0.5	−12.5	−16.5	331.7	329.0
19	150	150	15	0.75	5.2	6.0	349.0	350.8
20	150	150	15	0.75	4.4	6.0	346.6	350.8
21	100	100	24	0.5	−16.5	−15.9	323.2	323.3
22	100	200	24	0.5	−15.1	−12.6	326.7	328.6
23	200	100	24	0.5	4.8	4.7	353.6	352.7
24	200	100	24	1	8.8	7.6	358.4	356.4
25	200	200	24	0.5	8.9	8.1	355.0	358.1
26	100	200	24	1	−9.4	−6.2	340.3	339.7
27	150	150	15	0.75	7.9	6.0	354.7	350.8
28	200	200	24	1	12.9	11.0	364.9	361.8
29	200	200	6	1	5.1	7.0	348.3	349.1
30	200	100	6	1	4.4	3.6	346.2	343.8
31	150	150	10	0.75	4.1	4.4	350.1	348.1
32	150	150	24	0.75	7.2	6.3	355.2	350.9
33	150	150	36	0.75	0.7	1.8	340.4	342.0
34	100	100	10	1	−10.7	−11.5	337.5	336.7
35	100	200	10	1	−8.3	−8.1	340.2	342.0
36	200	200	48	0.25	−11.0	−11.5	336.1	333.1
37	200	200	48	0.5	−8.6	−6.9	338.2	338.6
38	200	200	48	1	−0.8	−4.0	341.3	342.3
39	200	200	48	1.5	−12.0	−9.6	335.4	336.4
40	200	200	48	2	−23.0	−23.6	321.1	321.1

the molar ratio of epoxy to primary amine groups from 0.25 to 1 resulted also in higher T_g values. A similar trend was also observed for the cross-linking of EJO with amines.[28] At a molar ratio larger than 1, the amine likely reacts with the ester group to form amides and free glycerol. The latter may act as a plasticizer and consequently lead to a reduction in the T_g.[38]

Regression Model for T_{onset}
The effect of process conditions of the T_{onset} can be described by a multivariable nonlinear regression model. A visualization of the effect of process variables on the T_{onset} is not shown here because similar trends were observed as in the case of T_g. Optimum conditions were observed for all the process variables

Table V. Thermal and Mechanical Properties of the Cross-Linked ERSO with TETA for Run 3,[a] Run 23,[b] and Run 28[c]

	Run 3 (T_g: 6.9°C)	Run 23 (T_g: 4.8°C)	Run 28 (T_g: 12.9°C)
Tensile strength (MPa)	1.42 ± 0.06	0.56 ± 0.03	1.77 ± 0.05
Strain at auto break (%)	156.9 ± 10.8	112.7 ± 4.9	199 ± 6.8
Modulus (MPa)	1.9 ± 0.10	0.87 ± 0.13	1.81 ± 0.06
Modulus (AutYoung) (MPa)	1.31 ± 0.05	0.96 ± 0.11	1.35 ± 0.07

[a] 150°C, 150 bar, 15 h, 0.75 : 1 molar ratio of epoxy to primary amine groups.
[b] 200°C, 100 bar, 24 h, 0.5 : 1 molar ratio of epoxy to primary amine groups.
[c] 200°C, 200 bar, 24 h, 1 : 1 molar ratio of epoxy to primary amine groups.

expect pressure. At the optimum conditions, the cross-link density is probably the highest, which results in higher T_g and T_{onset}.

Optimization

A numerical optimization function was used to predict the highest T_g for the cross-linked polymers within the range of variables used in this study. According to the model, the highest T_g (12°C) is attainable at a 1 : 1 molar ratio of epoxide to primary amine groups, 180°C and 200 bar for 21 h. The estimated T_{onset} at these conditions is 361°C. These conditions were used

for subsequent cross-linking reactions of the EOs with TETA with the objectives to determine thermal and mechanical properties of the cross-linked polymers and to identify structure–property relations.

Synthesis of Cross-Linked Polymers with TETA at Optimum Process Conditions

The synthesis of cross-linked polymers from ERSO, ESO, EPO, and EJO using TETA were carried out at the optimum conditions (180°C, 200 bar, 21 h, 1 : 1 molar ratio epoxy to primary amine groups) as predicted by the model (see previous section). A commercial epoxidized soybean oil (CESO) was also included as a reference. The reaction of ECO with TETA was not investigated as poor results were obtained in the screening experiments due to the low amount of reactive epoxide groups per triglyceride.
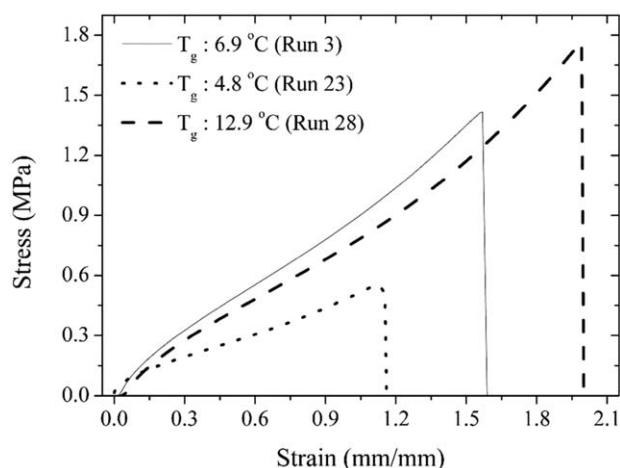
Table VII. ANOVA for the T_g of Cross-Linked Polymers from ERSO with TETA

	SS	DF	MS	F	p-value	R^2 values	
Model	3445	8	431	91.1	<0.0001	R^2	0.96
Error	151	31	5.2	1.9		$R^2_{adjusted}$	0.95
Total	3596	39				$R^2_{predicted}$	0.91

Figure 10. Strain–stress curves of polymers derived from the cross-linking of ERSO with TETA (refer to Table IV for the conditions of Run 3, Run 23, and Run 28).

Table VI. Coefficients for the Regression Model for T_g (°C)

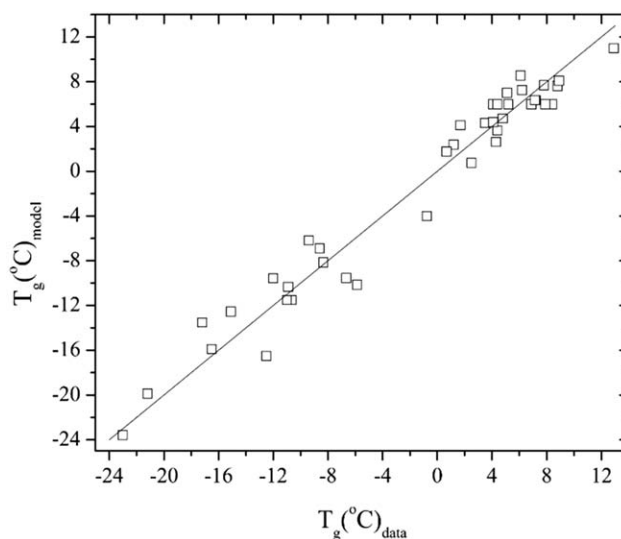| Variable	Coefficient
Constant	−121.57
T	1.07
P	0.03
t	0.82
R	45.06
T.R	−0.07
T^2	−0.003
t^2	−0.02
R^2	−16.91

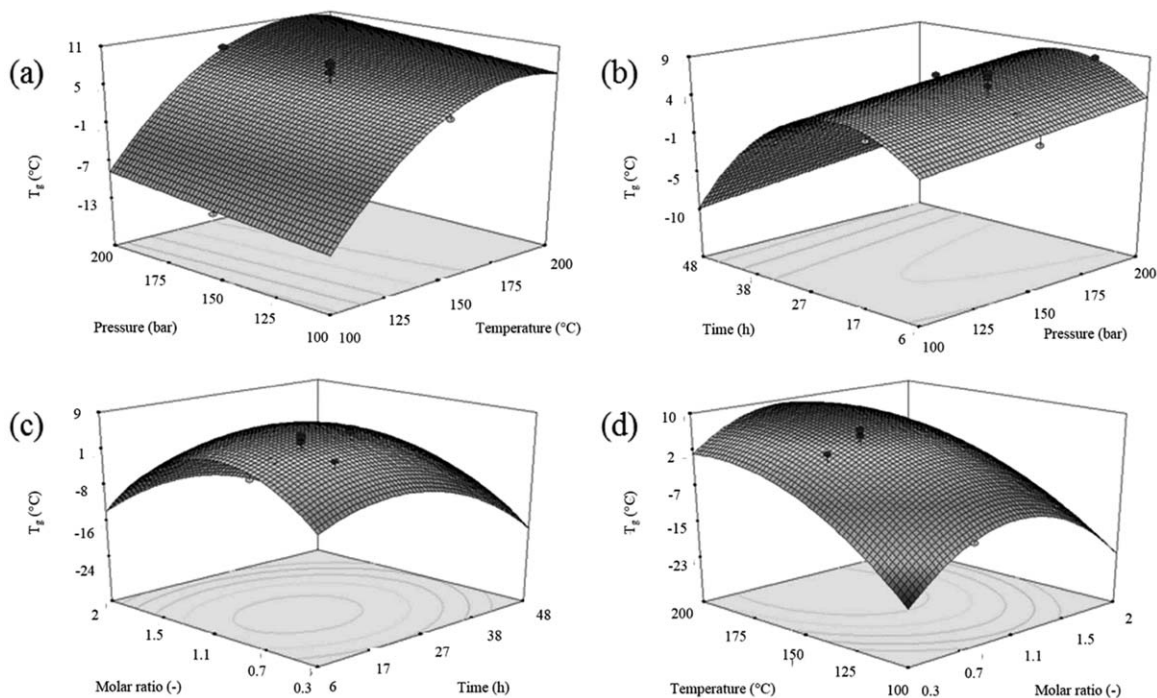**Figure 11.** Parity plot for the regression model of T_g.

Figure 12. Response surface showing the interaction between two parameters on the T_g (a) pressure and temperature (15 h, 1 : 0.75 molar ratio of epoxy to primary amine groups) (b) molar ratio of epoxy to primary amine groups and time (150°C, 150 bar)(c) time and pressure (150°C, 1 : 0.75 molar ratio of epoxy to primary amine groups) (d) temperature and molar ratio of epoxy to primary amine groups (150 bar, 15 h).

Thermal and Mechanical Properties of the Products

The thermal and mechanical properties of the cross-linked polymers were determined by DSC, TGA, and DMTA. The results are presented in Table VIII. The T_g of the polymers was determined by DSC. PEPO showed the lowest T_g (-1.6°C), PERSO the highest (11.1°C). These values are higher than those obtained in the screening experiments (refer to Table III for screening conditions). This is possibly due to higher temperature and pressure as well as longer curing time (180°C, 200 bar, 21 h). The T_g of PESO is slightly lower than that of the CESO based polymer (PCESO). This may be due to the slightly lower EOC of ESO (6.5%) as compared to the EOC of CESO (6.9%).

The regression model predicts that the T_g of PERSO is 12.0 ± 1.8°C. This nicely embeds the experimental value of 11.1°C. As such, the model gives a good prediction of the experimental dataset. The increase in the T_g when comparing PEPO and PERSO (-1.6 to 11.1°C) can be attributed to an increase in the degree of cross-linking, which was confirmed by DMTA measurements. The DMTA profiles of the polymers are given in Figure 13. The cross-linking density was estimated from the plateau storage modulus (E') and found to increase from PEPO (136 mol/m^3) to PERSO (494 mol/m^3) as shown in Table VIII. The thermal stability of the cross-linked polymers was determined by TGA. The onset of decomposition was between 340 and 360°C.

Tensile tests were performed to determine the mechanical properties of the cross-linked polymers and the results are shown in Figure 14 and Table VIII. The tensile strength varies between 0.18 and 1.72 MPa, whereas the modulus is in the range of 0.32–1.77 MPa. Resins with higher T_g values also show higher

Table VIII. Thermal and Mechanical Properties of Polymers Prepared at Optimum Conditions[a]

Polymer	T_g (°C)	T_{Max} (°C)	v (mol/m^3)	Tensile strength (MPa)	Strain at auto break (%)	Modulus (MPa)	Modulus (MPa) (AutYoung)
PERSO	11.1	486	494	1.72	182.4	1.77	1.29
PESO	6.1	487	322	1.03	136.7	1.24	1.18
PEJO	4.1	488	248	0.94	125.5	1.21	1.11
PEPO	−1.6	490	136	0.18	78.1	0.32	0.44
PCESO	6.9	489	373	1.11	145.7	1.28	1.17
Soybean oil based[27]	9.8	511	486	1.34			
Jatropha oil based[28]	8.7			0.82	86.9	1.6	

[a] 180°C, 200 bar, 21 h, 1 : 1 molar ratio epoxy to primary amine groups.

strengths and modulus. A similar trend was observed for the strain at break, see Table V for details. This is likely because at $T_g \pm 10°C$, higher tensile strength can be coupled, as reported[27] with higher strain at break.

The T_g of PEJO (4.1°C) is lower than previously reported by our group (8.7°C). This may be due to a lower temperature and shorter pre-mixing time (100°C and 0.5 h as compared to 150°C and 2 h) during the synthesis. These conditions were selected to reduce the level of amidation, which is more prominent at higher temperature and longer premixing times (Figures 5 and 7).

PERSO has the highest the cross-link density (494 mol/m^3), see Table VIII for details. Soybean oil based polymer (PESO and PCESO) have a cross-link density in the range of 322–373 mol/m^3. These values are lower than those reported for azidated soybean oil alkynated with soybean oil (486 mol/m^3). Low cross-link densities are also observed for PEJO (248 mol/m^3) and PEPO (136 mol/m^3). This may be due to the lower amounts of epoxy groups in the EOs leading to a denser cross-linked network and consequently a lower cross-linked density.

In brief, we have shown that PERSO has a higher T_g and tensile strength compared to PESO, PEJO, and PEPO resins. This may be due to the relatively high level of epoxidation. The T_g of PERSO (<30°C) indicates that the product may find applications in the field of adhesives in the electronic and automotive sector. If necessary, other cross-linkers may be used instead of TETA to give product with a higher T_g and thus a higher modulus and strength.

CONCLUSIONS

RSO was successfully epoxidized using performic acid (generated *in situ*) resulting in epoxidized rubber seed oil with a high EOC value (7.4%). ERSO was cross-linked with TETA and the optimum conditions for high T_g were determined. At the optimum conditions (180°C, 200 bar, 21 h, 1 : 1 molar ratio of epoxy to primary amine groups), the cross-linked material (PERSO) has a T_g of 11.1°C with a tensile strength of 1.72 MPa and an elongation at break of 182%. These values are higher
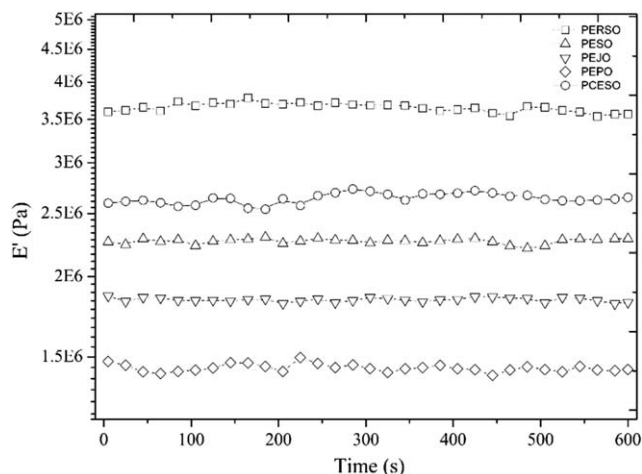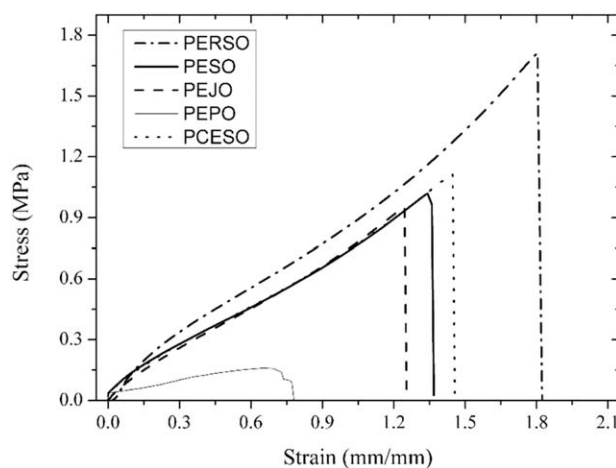

Figure 14. Strain–stress curves of polymers derived from the cross-linking of EOs with TETA.

than for the resin obtained by reacting commercial epoxidized soybean oil with TETA at similar conditions (T_g of 6.9°C, tensile strength of 1.11 MPa and strain at auto break of 145.7%). This indicates that RSO is a promising raw material for the synthesis of renewable epoxy type resin. RSO is particularly attractive as it has a relatively high content of unsaturated fatty acids compared to, e.g., jatropha and soybean oil.

This study confirms that the seeds of the rubber tree have good potential for further valorization and that other applications, besides the use of the oil as a biofuel, seem viable.

ACKNOWLEDGMENTS

Figure 13. DMTA curves for polymers derived from the cross-linking of EOs with TETA.

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