

# Cross-linking of Epoxidised Rubber Seed Oil With Triethylenetetramine To Produce Novel Resins

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Epoxidised oil with an epoxy content of 7.4 wt% were prepared from rubber seed oil. Bulk polymerisation/curing of the epoxidised oils with triethylenetetramine (in the absence of a catalyst) was carried out in a batch set-up (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 modelled using multi variable non-linear regression. The rubber seed oil-derived polymer has a glass transition temperature of 11.1 °C, a tensile strength of 1.72 MPa and strain at break of 182 %. These results highlights the potential of rubber seed oil as a source for novel resins at industrial/commercial level.

**Keywords:** *Cross-linking, epoxidation, resin, rubber seed oil, triethylenetetramine.*

## I. INTRODUCTION

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 [1]. Epoxidised plant oils are attractive starting materials for advanced materials and are already available on industrial scales and widely used as plasticizers and stabilizers for the production of polyvinyl chloride (PVC) [2-4].

A potentially very attractive plant oil for the synthesis of advanced materials is the oil from 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 [5, 6]. In this study, we report our findings on the epoxidation of RSO oil and the subsequent application of the epoxidised rubber seed oil as a starting material for the synthesis of novel resins.

## II. MATERIALS AND METHODS

### 1. Materials

The RSO oil was obtained by pressing rubber seeds from Bengkulu, Indonesia using a standard hydraulic press. Hydrogen peroxide (30 wt%, pro analysis), triethylenetetramine (97%) and  $\text{CDCl}_3$  (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.

### 2. Epoxidation of RSO

The ERSO 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 minutes. Afterward, the mixture was poured into a steel mold plate (100 x 100 x 1 mm<sup>3</sup>) and pressed at 100-200 bar and 100-200 °C (Schwabenthan Polystat 100T) at different pressing times (6-48 h).

RSO 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.  $\text{H}_2\text{O}_2$  (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 epoxidised RSO (ERSO) 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 vacuum distillation (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 analysed by <sup>1</sup>H-NMR and FT-IR. The epoxide conversion for RSO is approximately 97 mol%.

### 3. Cross-linking of ERSO with triethylenetetramine (TETA)

The ERSO 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 minutes. Afterward, the mixture was poured into a steel mold plate (100 x 100 x 1 mm<sup>3</sup>) and pressed at 100-200 bar and 100-200 °C (Schwabenthan Polystat 100T) at different pressing times (6-48 h).

## III. RESULTS AND DISCUSSION

### 1. Synthesis of ERSO

Epoxidation experiments with RSO were carried out in a batch set-up using a carbon-carbon double bonds to formic acid to hydrogen peroxide molar ratio of 1:4:25 at 60 °C [7]. The batch time was varied from 1-12 h to determine the carbon-carbon double bond conversion as a function of the batch time (<sup>1</sup>H-NMR). 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.

### 2. Synthesis of cross-linked polymers

The cross-linking experiments of ERSOs with TETA were carried a batch set-up followed by casting of the mixture in a steel mold. Experiments were carried out at conditions close to those previously used in our group for the cross-linking of epoxidised jatropha oil with TETA [7] and involves an initial reaction/pre-mixing in a batch set-up (variable molar ratio of epoxide to amine primary groups, 100 °C, 100 rpm, 30 min) followed by casting of the mixture in a steel mold at different process conditions

(Table 1) and the results are shown in Table 2.

Table 1 Experimental conditions for the synthesis of cross-linked polymers from ERSO with TETA

Variable	Range
Mold temperature (°C)	100-200
Mold pressure (bar)	100-200
Pressing time (h)	6-48
Molar ratio of epoxy to primary amine functional group (-)	0.25-2

Table 2 Thermal and Mechanical properties of cross-linked polymers from ERSO with TETA<sup>a)</sup>

Properties	Value
T <sub>g</sub> (°C)	11.1
Cross-link density (mol/m <sup>3</sup> )	494
Tensile strength (MPa)	1.72
Strain at auto break (%)	182.4
Modulus (MPa)	1.77
Modulus (AutYoung) (MPa)	1.29

<sup>a)</sup> 180 °C, 200 bar, 21 h, 1:1 molar ratio of epoxy to primary amine groups

The effect of process conditions of the T<sub>g</sub> can be described by a multi-variable non-linear regression model. Optimum conditions were observed for all the process variables expect pressure. At the optimum conditions (180 °C, 200 bar, 21 h, 1:1 molar ratio of epoxy to primary amine groups), the cross linked material has a T<sub>g</sub> of 11.1 °C with a tensile strength of 1.72 MPa and an elongation at break of 182 %.

## IV. CONCLUSIONS

The RSO was successfully epoxidised using performic acid (generated *in situ*) resulting in epoxidised rubber seed oil with a high EOC value (7.4 wt%). ERSO was cross-linked with TETA and the optimum conditions for high T<sub>g</sub> 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<sub>g</sub> of 11.1 °C with a tensile strength of 1.72 MPa and an elongation at break of 182 %. These values are higher than for the resin obtained by reacting commercial epoxidised soybean oil with TETA at similar conditions (T<sub>g</sub> 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.

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