Journal of Oil Palm Research Vol. 27 (1) March 2015 p. 39-56

NOVEL HIGH MOLECULAR WEIGHT POLYMERS BASED ON PALM OIL

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ABSTRACT

Palm oil possesses, on average, about 1.8 double bonds per triglyceride. As a result of the relatively low level of unsaturation associated with palm oil, the ability to produce useful thermoset materials is limited. As a means to overcome this limitation, a novel palm oil-based monomer and polymer were produced. The monomer was produced by base-catalysed transesterification of palm oil with 2-(vinyloxy) ethanol. This monomer was subsequently polymerised using cationic polymerisation to produce a polymer with a number-average molecular weight of approximately 20 000 g mole^{-1}*. The cationic polymerisation process utilised enabled selective polymerisation through the vinyl ether groups. With this polymerisation process, the unsaturation derived from the palm oil was preserved and utilised for crosslinking. For example, the polymer produced was epoxidised and the epoxide groups subsequently ring-opened with methanol to produce a polymeric polyol. Due to the relatively higher number of hydroxyl groups per molecule associated with the palm oil-based polyvinyl ether polyol, tough, hard polyurethane coatings were produced that cured relatively quickly. Details related to monomer synthesis and characterisation, polymer synthesis and characterisation, polymer derivatisation and characterisation, and thermoset network production and characterisation are presented.*

Keywords: palm oil, vinyl ether, polymer, urethane, coating, biobased.

Date received: 11 April 2014**; Sent for revision:** 6 August 2014**; Received in final form:** 19 November 2014; **Accepted:** 5 January 2015.

INTRODUCTION

Plant oils represent very useful renewable building blocks for the production of thermoset materials. The oils are relatively easy to extract and possess a number of functional groups that can be utilised to derivatise the molecules for application in a wide variety of applications and curing chemistries (Biermann *et al.*, 2000; Guner *et al.*, 2006; Meier *et al.*, 2007; Ronda *et al.*, 2011). *Figure 1* provides a representative triglyceride from a plant oil and identifies different sites that can be used for derivatisation. The carbonyl carbon of the ester functional group (*b* in *Figure 1*) is susceptible to reactions with nucleophiles, such as alcohols and amines, while the allylic (*c* in *Figure 1*) and bis-allylic (*e* in *Figure 1*) hydrogens are susceptible to abstraction by free radicals and cations. The double bonds (*d* in *Figure 1*) are susceptible to a variety of addition reactions involving a free radical or cationic mechanism. The hydrogen atoms attached to the carbons alpha to the carbonyl (*f* in *Figure 1*) are susceptible to abstraction by anionic species, while the hydrogens atoms on the carbon next to the ester

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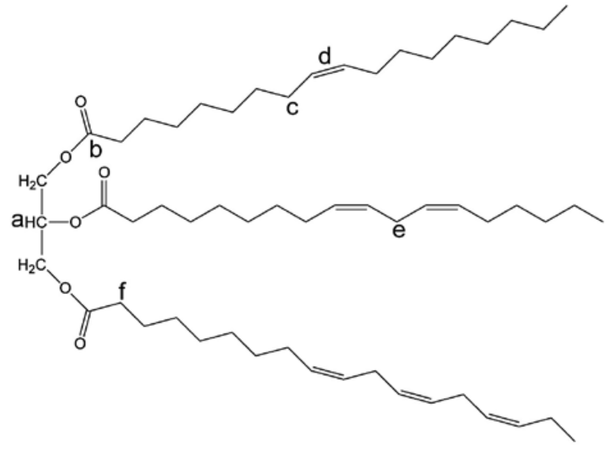

Figure 1. A representative plant oil triglyceride with the different reactive sites for derivatisation identified.

group (*a* in *Figure 1*) can be abstracted by free radicals. Probably the most widely used derivatisation method utilised for the production of plant oil-based materials for the production of thermoset networks involves epoxidation of the double bonds (Baumann *et al*., 1988). Epoxidised plant oils have been used to generate thermoset coatings using the common methods of curing epoxide-functional resins such as with amines (Liu *et al*., 2002; 2004), anhydrides (Gerbase *et al*., 2002), and cationic photocure (Thames and Yu, 1999; Thames *et al*., 2000; Wan Rosli *et al*., 2003). Epoxidised plant oils have been further derivatised by reaction of the epoxide groups with acrylic acid to produce acrylate-functional plant oils (Fu *et al*., 2010; Li *et al*., 2010). Similar to other liquid, multifunctional acrylates, acrylate-functional plant oils have been used in radiation-curable coatings (Bajpai *et al*., 2004; Dzunuzovic *et al*., 2005). In addition to serving as a starting material for the generation of acrylate-functional plant oils, epoxidised plant oils have been used to generate plant oil-based polyols by reaction of the epoxide groups with, for example, methanol (Zlatanic *et al*., 2004). These polyols can be formulated with isocyanates to produce polyurethane coatings (Javni *et al*., 2003; Zlatanic *et al*., 2004).

The utility of any given plant oil for use in thermoset materials is highly dependent on the chemical composition of the fatty acid ester alkyl groups. In particular, the level of unsaturation is critical for derivatives produced using double bond epoxidation as a primary method of functionalisation. To illustrate, the average number of double bonds per triglyceride for a representative drying, semi-drying, and non-drying oil can be considered. The average number of double bonds for linseed oil (drying oil), soyabean oil (semi-drying oil), and palm oil (non-drying oil) is 6.3, 4.6, and 1.8, respectively. Considering these numbers, it can be easily understood that, all else being equal, the crosslink density of networks derived from these three different plant oils will be very different. Since many properties of a thermoset material, such as modulus, elasticity, hardness, and chemical resistance, are highly dependent on crosslink density, the choice of a particular plant oil starting material will be very important for meeting the requirements of a specific application.

The authors have been heavily involved in the production of plant oil-based polyvinylethers that enable the number of double bonds per molecule to be dramatically increased over the parent plant oil (Alam and Chisholm, 2011; Chernykh *et al*., 2013). In addition, the technology enables copolymerisation, which can be used to widely tailor many materials properties (Alam *et al*., 2013). Initial work was focused on using soyabean oil as the plant oil-based starting material, and it was extensively demonstrated that incorporating the soyabean oil-derived fatty acid ester alkyl groups as pendant chains to the polyvinylether backbone dramatically reduced cure times and increased crosslink density compared to analogous derivatives based on the parent soyabean oil (Alam and Chisholm, 2011). The objective of the work described in this document was to investigate the production of polyvinylethers possessing pendant groups derived from palm oil (PO). In addition, the work provides preliminary information on the functionalisation of a PO-based polyvinylether to produce a polyol that was subsequently used to produce polyurethane networks.

EXPERIMENTAL

Materials

Table 1 provides a description of the starting materials used for the study. Unless specified otherwise, all materials were used as received from the vendor.

Synthesis of the Palm Oil-based Vinyl Ether Monomer, 2-(Vinyloxy)ethyl Palmitate

The vinyl ether monomer derived from palm oil, which is being referred to as 2-(vinyloxy)ethyl palmitate (2-VOEP), was synthesised as follows: KOH (4.5 g) was first heated at 140°C for 30 min to remove adsorbed moisture and then cooled down to room temperature under a nitrogen atmosphere. PO (163 g) was deaerated by bubbling with nitrogen for 30 min at 40°C. The dried KOH and deaerated PO were charged to a 1 litre round bottom flask (RBF) equipped with a condenser, magnetic stirrer, oil bath, and nitrogen inlet and outlet. To this solution, 2-HEVE (163 g) was added and the rapidly stirring solution heated to 70°C under a nitrogen atmosphere for 3 hr. The reaction mixture was cooled

TABLE 1. A DESCRIPTION OF THE MATERIALS USED FOR THE STUDY

Chemical	Designation	Vendor
Palm oil	PO	Malaysian Palm Oil Board
Epoxidised soyabean oil	ESBO	Arkema Inc.
2-Hydroxy ethyl vinyl ether, >95%	2-HEVE	TCI America
Potassium hydroxide	KOH	Sigma-Aldrich
n-Hexane	*n*-Hexane	Sigma-Aldrich
Magnesium sulphate	$MgSO_4$	Sigma-Aldrich
Ethylaluminum sesquichloride, 97%	$Et_3Al_2Cl_3$	Sigma-Aldrich
Methanol, 98%	Methanol	BDH Chemicals
Acetic acid	Acetic acid	Sigma-Aldrich
Acidic ion-exchange resin	Amberlite® IR-120H	Sigma-Aldrich
Hydrogen peroxide (50 wt% in water)	H_2O_2	Sigma-Aldrich
Ethyl acetate	Ethyl acetate	BDH Chemicals
Sodium bicarbonate, ACS grade	$NaHCO_3$	Amresco Inc.
Tetrafluoro boric acid, 48 wt% in water	HBF_4	Sigma-Aldrich
Ammonium hydroxide solution	NH_4OH	Sigma-Aldrich
Toluene	Toluene	BDH Chemicals
Tolonate® HDT 90 (hexamethylene diisocyanate trimer)	HDT	Perstorp
Dibutyltin dilaurate, 95%	DBTDL	Sigma-Aldrich
Tetrahydrofuran, 99.0%	THF	J.T.Baker
Methyl ethyl ketone	MEK	Alfa Aesar

to room temperature and then transferred to a 2 litre separating funnel. Next, 1 litre of *n*-hexane was added and the resulting solution washed three times with 300 ml of acidic water (pH 3.5-4), two times with deionised (DI) water (300 ml), and, finally, with brine solution (300 ml). The *n*-hexane layer was dried with $MgSO_4$ and solvent removed under vacuum at 35ºC and 100 mbar pressure. The chemical composition of the product was confirmed using proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform infrared spectroscopy (FTIR).

Synthesis of Poly[2-(vinyloxy)ethyl palmitate]

The cationogen, 1-isobutoxyethyl acetate (IBEA), was synthesised using a procedure described elsewhere (Aoshima and Higashimura, 1989). The polymerisation of 2-VOEP was carried out inside a dry nitrogen glove box in a 1000 ml RBF that was baked at 200ºC prior to use and equipped with an overhead mechanical stirrer. The 2-VOEP (70 g) and IBEA (165 mg) were dissolved in toluene (420 ml) that had been dried over calcium hydride and the solution chilled to 0ºC using a heptane bath. The polymerisation was initiated by the addition of 5.65 ml of the co-initiator, $Et_3Al_2Cl_3$ (25 wt% in toluene). The polymerisation was terminated after 18 hr by the addition of 420 ml of chilled methanol. In addition to terminating the polymerisation, the methanol caused the polymer to precipitate. The precipitate was isolated by decanting off the majority of the liquids and then purified by re-dissolving in dichloromethane, re-precipitating into methanol, and decanting off most of the liquids. The purified polymer was collected as a viscous liquid after drying under vacuum (35 mbar pressure) overnight at 35ºC. The chemical composition of the product was confirmed using ^{1}H NMR and FTIR.

Synthesis of the Polyol of Poly[2-(vinyloxy)ethyl palmitate]

The polyol of poly(2-VOEP) [HO-poly(2-VOEP)] was produced using a common route for the production of plant oil-based polyols, which involved the production and isolation of an epoxide-functional derivative and subsequent ring-opening of the epoxy groups to produce secondary hydroxyl groups. The epoxidised derivative of poly(2-VOEP) [E-poly(2-VOEP)] was synthesised as follows: to a 250 ml, two-neck RBF equipped with a condenser and an addition funnel, poly(2-VOEP) (35 g), acetic acid (1.85 g), and Amberlite® IR-120H (7 g) were combined and mixed well. The H_2O_2 (11 ml, 50%) was added dropwise via the addition funnel and the reaction temperature maintained at 60ºC for 5 hr. After this period, the reaction mixture was allowed to cool to room temperature, transferred to a 500 ml separating funnel, and the bottom layer discarded. Next, 200 ml of ethyl acetate was added to the separating funnel and the resulting solution washed three times with saturated $NaHCO_3$ solution (100 ml), followed by a brine wash (100 ml), and a final wash with DI water (100 ml). The ethyl acetate layer was dried with $MgSO_4$ and then the solvent was removed at 35ºC using 35 mbar of pressure.

From E-poly(2-VOEP), HO-poly(2-VOEP) was produced as follows: in a two-neck, 250 ml RBF equipped with a condenser and an addition funnel, methanol (14 ml) and tetrafluoroboric acid (0.4 ml) were added and mixed well. Next, a solution of E-poly(2-VOEP) (25 g) in toluene (75 ml) was added dropwise over the course of 30 min via the addition funnel and the reaction temperature maintained at 50ºC. The reaction was carried out at 50ºC for 1 hr before terminating the reaction with 1 ml of NH_4OH solution. The reaction mixture was allowed to cool to room temperature and then transferred to a 500 ml separatory funnel. Next, 200 ml of *n*-hexane was added to the separatory funnel and the resulting solution washed two times with DI water (100 ml), followed by a brine wash (100 ml). The *n*-hexane layer was dried with $MgSO_4$ and then the solvent was removed at 35ºC using 100 mbar of pressure.

Synthesis of the Polyol of Palm Oil

The polyol of PO (HO-PO) was synthesised using essentially the process as that used to produce HO-poly(2-VOEP). Epoxidation of PO was achieved as follows: to a 250 ml, two-neck RBF equipped with a condenser and an addition funnel, PO (50 g), acetic acid (3.2 g), and Amberlite® IR-120H (10 g) were combined and mixed well. The H_2O_2 (16 ml, 50%) was added dropwise via the addition funnel and the reaction temperature maintained at 60ºC for 5 hr. After this period, the reaction mixture was allowed to cool to room temperature, transferred to a 500 ml separating funnel, and the bottom layer discarded. Next, 300 ml of ethyl acetate was added to the separating funnel and the resulting solution washed three times with saturated $NaHCO_3$ solution (150 ml), followed by a brine wash (150 ml), and a final wash with DI water (150 ml). The ethyl acetate layer was dried with $MgSO_4$ and then the solvent was removed at 35ºC using 35 mbar of pressure. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 5.15-5.25 (m, 1H, -O-CH$_2$-C*H*-), 4.05-4.35 (dd, dd, -O-C*H*$_2$-CH-C*H*$_2$-O-), 2.75-3.15 (m, 3.5H, -CH(O)CH-), 2.20-2.35 (t, 6H,-C=0C*H*$_2$-), 1.15-1.75 (m, 78H,-C=0CH$_2$C*H*$_2$-; -CH$_2$C*H*$_2$CH$_2$-; -CH(O)C*H*$_2$CH$_2$-; -CH(O) C*H*$_2$CH(O)-), 0.75-0.95 (m, 9H, -CHC*H*$_3$).

From the epoxidised PO, HO-PO was produced as follows: in a two-neck, 250 ml RBF equipped with a condenser and an addition funnel, methanol (15 ml) and tetrafluoroboric acid (0.5 ml) were added and mixed well. Next, a solution of epoxidised PO (30 g) in toluene (75 ml) was added dropwise over the course of 30 min via the addition funnel and the reaction temperature maintained at 50ºC. The reaction was carried out at 50ºC for 1 hr before terminating the reaction with 1.2 ml of NH_4OH solution. The reaction mixture was allowed to cool to room temperature and then transferred to a 500 ml separatory funnel. Next, 200 ml of n-hexane was added to the separatory funnel and the resulting solution washed two times with DI water (100 ml), followed by a brine wash (100 ml). The *n*-hexane layer was dried with $MgSO_4$ and then the solvent was removed at 35ºC using 1 mbar of pressure. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 5.15-5.25 (m, 1H, -O-CH$_2$-C*H*-), 4.05-4.35 (dd, dd, -O-C*H*$_2$-CH-C*H*$_2$-O-), 3.23-3.21, 3.39-3.49 (m, 1.5, -CH-O*H*; -C*H*-OH), 3.33-3.39 (s, 3.6, -OC*H*$_3$), 2.9-3.0 (q, 1.2, -CH$_3$-O-C*H*-), 2.20-2.35 (t, 6H,-C=0C*H*$_2$-), 1.0-1.7 (m, 78, -C=0CH$_2$C*H*$_2$-; -CH$_2$C*H*$_2$CH$_2$-; -CH$_3$-O-CH-C*H*$_2$-; -HO-CH-C*H*$_2$-), 0.75-0.95 (m, 9H, -CHC*H*$_3$).

Synthesis of the Polyol of Soyabean Oil

From the commercially available ESBO, HO-SBO was produced as follows: In a two-neck, 250 ml RBF equipped with a condenser and an addition funnel, methanol (35 ml) and tetrafluoroboric acid (2.3 g) were added and mixed well. Next, a solution of epoxidised SBO (50 g) in toluene (300 ml) was added dropwise over the course of 30 min via the addition funnel and the reaction temperature maintained at 50ºC. The reaction was carried out at 50ºC for 1 hr before terminating the reaction with 4.5 ml of NH_4OH solution. The reaction mixture was allowed to cool to room temperature and then transferred to a 500 ml separatory funnel. Next, 300 ml of *n*-hexane was added to the separatory funnel and the resulting solution washed two times with DI water (150 ml), followed by a brine wash (150 ml). The *n*-hexane layer was dried with $MgSO_4$ and then the solvent was removed at 35ºC using 1 mbar of pressure. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 5.15-5.25 (m, 1H, -O-CH$_2$-C*H*-), 4.05-4.35 (dd, dd, -O-C*H*$_2$-CH-C*H*$_2$-O-), 3.23-3.49 (m, -CH-O*H*; -C*H*-OH; -OC*H*$_3$), 2.9-3.0 (q, 3.6, -CH$_3$-O-C*H*-), 2.20-2.35 (t, 6H,-C=0C*H*$_2$-), 1.0-1.7 (m, 65, -C=0CH$_2$C*H*$_2$-; -CH$_2$C*H*$_2$CH$_2$-; -CH$_3$-O-CH-C*H*$_2$-; -HO-CH-C*H*$_2$-), 0.75-1.00 (m, 9H, -CHC*H*$_3$).

Preparation of Polyurethane Free Films and Coatings

Polyurethane free films and coatings were prepared using three different polyols and the trifunctional isocyanate, HDT. The molar ratio of OH functionality to NCO functionality was 1.0/1.1. The composition of the liquid mixtures used to produce the polyurethanes is provided in *Table 2*. The

TABLE 2. THE COMPOSITIONS OF LIQUID MIXTURES USED TO PRODUCE POLYURETHANE NETWORKS*

Component	HO-PO/HDT	HO-SBO/HDT	HO-poly(2-VOEP)/HDT
HO-PO	8.00	-	-
HO-SBO	-	8.09	-
HO-poly(2-VOEP)	-	-	7.95
HDT	3.73	7.03	3.02
Toluene	-	-	2.00
DBTDL†	0.29	0.37	0.27

Note: * All values are in grammes. †A stock solution of DBTDL in toluene was prepared by mixing 0.124 g in 15 g of toluene.

mixtures were thoroughly blended using a FlackTek mixer operating at 3500 rpm for 30 s. Each coating solution was coated on nine steel-Q panels, one glass panel, and one Teflon®-laminated glass panel using a drawdown bar. The coated panels were cured at 100ºC for 14 hr. Coating on the Teflon®-laminated glass panel allowed for free film samples to be produced for the characterisation of mechanical and viscoelastic properties as well as gel content.

Instrumentation

A JEOL-ECA 400 (400 MHz) nuclear magnetic resonance spectrometer equipped with an autosampler was used to generate ^{1}H NMR spectra. Data acquisition was completed using 16 scans in $CDCl_3$ as the lock solvent. FTIR was conducted using a Nicolet 6700 FTIR spectrometer. Samples were prepared by coating a thin layer of liquid on a KBR plate. Spectra were recorded using 64 scans and 4 cm^{-1} resolution with a data spacing of 0.964 cm^{-1}. Molecular weight and molecular weight distribution of poly(2-VOEP) was determined by using a high-throughput Symyx Rapid GPC. The instrument was equipped with an evaporative light-scattering detector (PL-ELS 1000) and 2xPLgel Mixed B column (10 μm particle size). Polymer solutions were prepared by dissolving 20 mg samples in 6 ml of THF.

Thermal properties of the polymers were characterised using differential scanning calorimetry (DSC). The instrument was a Q1000 DSC from TA Instruments, and sample sizes ranged from 6 to 10 mg. Samples were cooled down to -90ºC from room temperature (first cooling cycle), held at -90ºC for 3 min, heated from -90ºC to 50ºC (first heating cycle), held at 50ºC for 3 min, cooled down to -90ºC (second cooling cycle), and reheated to 80ºC (second heating cycle). With the exception of the first heating cycle, the heating and cooling rate for all cycles was 10ºC min^{-1}. The heating rate for the first heating cycle was 5ºC min^{-1}.

The thickness of cured coatings was determined using a PosiTest DFT® dry-thickness measurement gauge from DeFlesko Corporation. Viscoelastics properties of free film specimens were characterised using a Q800 Dynamic Mechanical Analyser from TA Instruments over a temperature range of -90°C to 150°C. The heating rate, frequency, and strain amplitude utilised was 5°C min^{-1}, 1 Hz, and 0.02%, respectively. Mechanical properties of free film specimens were determined using an Instron 5545 Tensile Tester fitted with a 100 N load cell. Cure kinetics were characterised with an ARES Rheometer from TA Instruments. Liquid samples were placed in between parallel plates with a gap of 0.53 mm and complex viscosity recorded as a function of time at a temperature of 100°C, frequency of 10 rad s^{-1}, and strain of 0.5%.

Characterisation Methods

Chemical resistance was accessed using ASTM D 5402-93, which is typically referred to as the methyl ethyl ketone (MEK) double-rub test. The hardness of the coatings was accessed using the König pendulum hardness test (ASTM D 4366-95), while the impact resistance of coated panels was accessed using ASTM D 2794-93. Mechanical properties were obtained from 'dumb bell'-shaped free-film specimens produced using a die cutter and the procedure outlined in ASTM D 638–5. The displacement rate of the movable clamp was set as 1 mm min^{-1}. The data reported was the average of four replicate measurements. The flexibility of coatings on steel substrates was characterised using the mandrel bend test (ASTM D 522-93a). The gel content of free films was determined gravimetrically by measuring the weight of specimens (approximately 1 g) before and after soxhlet extraction. The soxhlet extraction was done using toluene as the solvent and an extraction time of 4 hr. Prior to weighing samples, they were dried overnight in a vacuum oven operating at 1 mbar pressure and 50°C.

RESULTS AND DISCUSSION

Synthesis and Characterisation of 2-(Vinyloxy) Ethyl Soyate (2-VOEP)

The 2-VOEP was synthesised using base-catalysed transesterification, as shown in *Figure 2*. The process is very similar to the process used to produce biodiesel with the exception that 2-HEVE is used in place of methanol or ethanol. The water-solubility of 2-HEVE was high enough that it could be easily removed along with glycerol by a simple aqueous/organic separation. The purified monomer is a crystalline solid with a melting temperature of 28°C. *Figures 3* and *4* provide the ^{1}H NMR and FTIR spectra for 2-VOEP, respectively. As shown in *Figure 3*, the vinyl protons associated with the internal double bonds derived from PO and the terminal vinyl ether double bond derived from 2-HEVE are nicely separated. From the FTIR spectrum, characteristic bands associated with the expected chemical structure for 2-VOEP can be observed. For example, the strong band centred at 1752 cm^{-1} is due to carbonyl stretching, while bands centred at 1617 cm^{-1} (C=C stretching), 985 cm^{-1} (*trans* CH wag), and 819 cm^{-1} (terminal CH_2 wag) are the result of the vinyl ether double bond (Silverstein *et al.*, 1981). The intense bands centred at 2850 cm^{-1} and 2920 cm^{-1} are due to CH_2 stretching motions, while the weak shoulder at 3005 cm^{-1} is due to motions of the CH olefin groups of the internal double bonds derived from PO.

Synthesis and Characterisation of Poly [2-(vinyloxy) ethyl palmitate]

Poly(2-VOEP) was synthesised using the cationic polymerisation system that was previously used to polymerise an analogous vinyl ether monomer derived from soyabean oil [*i.e.* 2-(vinyloxy)ethyl soyate (2-VOES)] (Alam and Chisholm, 2011). This particular cationic polymerisation system was shown to provide polymerisation exclusively through the vinyl ether double bonds, which enabled the production of linear polymers to be produced that retained all of the double bonds derived from soyabean oil. In addition, polymerisation of 2-VOES with this system was demonstrated to provide a living polymerisation (Chernykh *et al.*, 2013). The production of a living polymerisation provides for polymers with a relatively narrow molecular weight distribution, control of polymer molecular weight, and the potential to create polymers with controlled architectures, such as block copolymers, multi-arm star polymers, telechelic polymers, and graft copolymers (Webster, 1991).

Figure 5 illustrates the polymerisation process that was used to polymerise 2-VOEP. With this polymerisation system, initiation is obtained by ionisation of the carbon-oxygen single bond associated with the C-O(C=O)CH_3 group of the cationogen, IBEA, by complexation of the ester group with the coinitiator, $Et_3Al_2Cl_3$. Although the authors have not yet conducted the appropriate polymerisation studies to determine if the

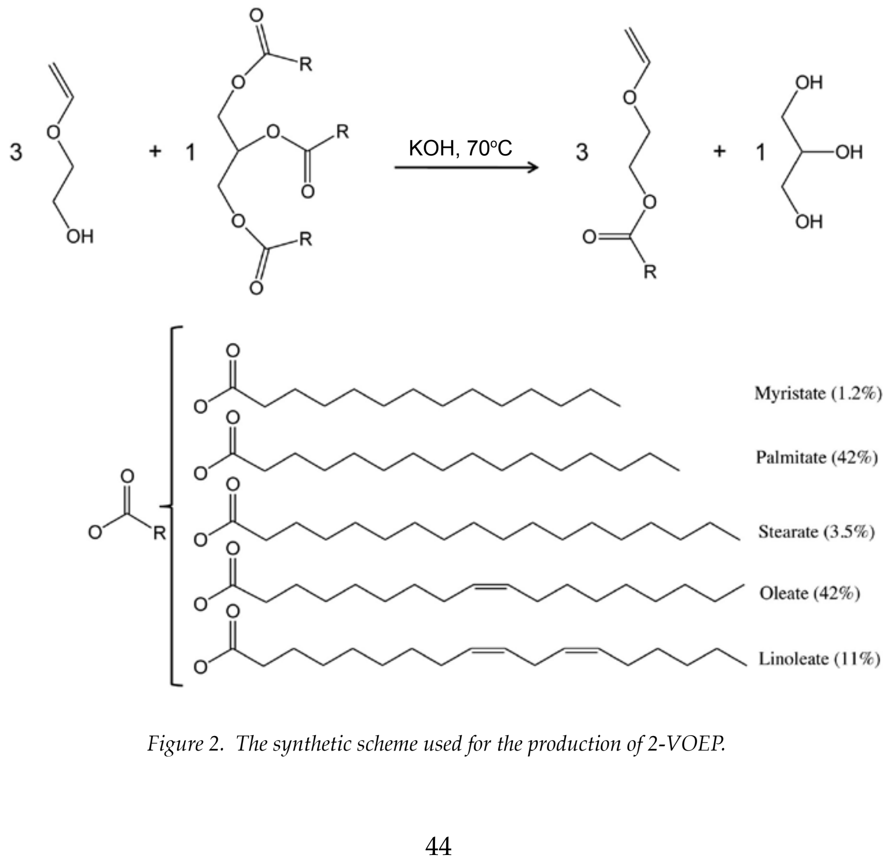

Figure 2. The synthetic scheme used for the production of 2-VOEP.

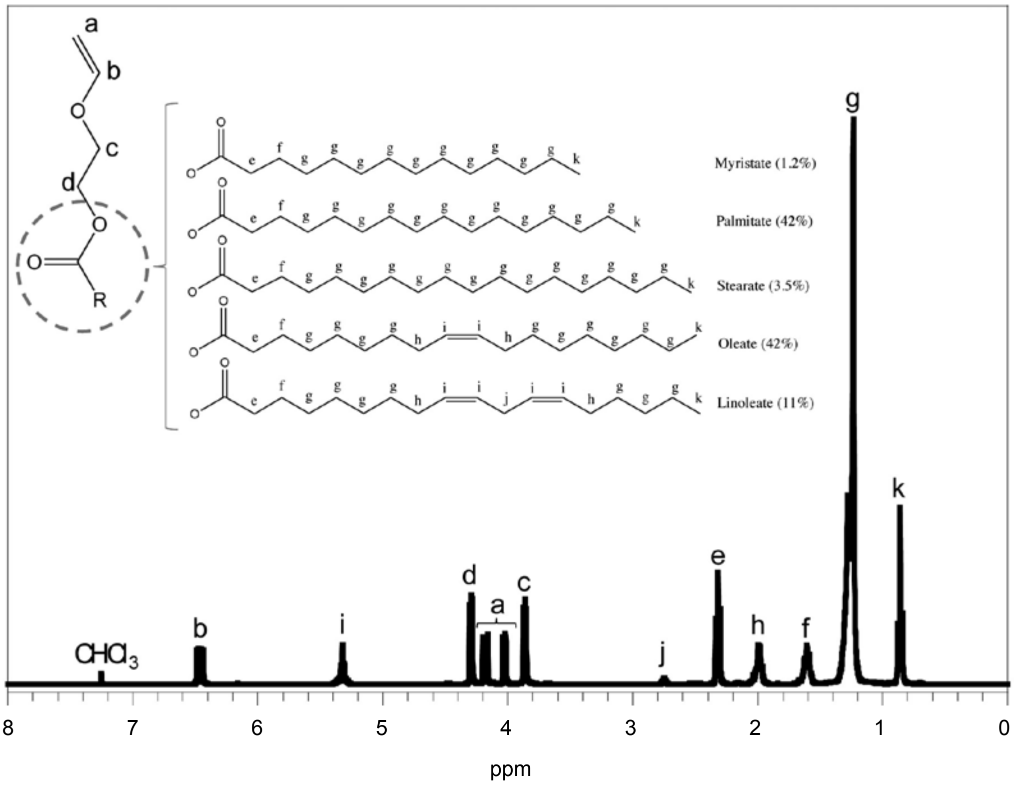

Figure 3. The ^{1}H NMR spectrum obtained for 2-VOEP.

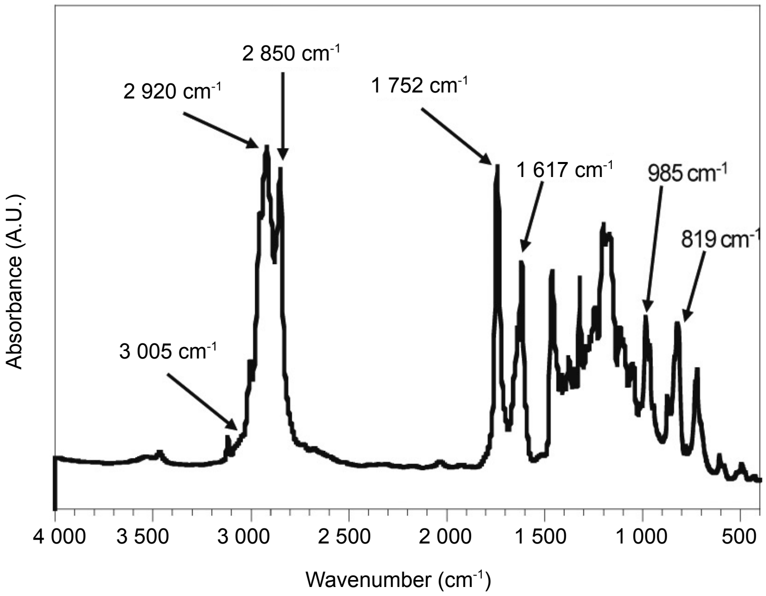

Figure 4. The FTIR spectrum obtained for 2-VOEP.

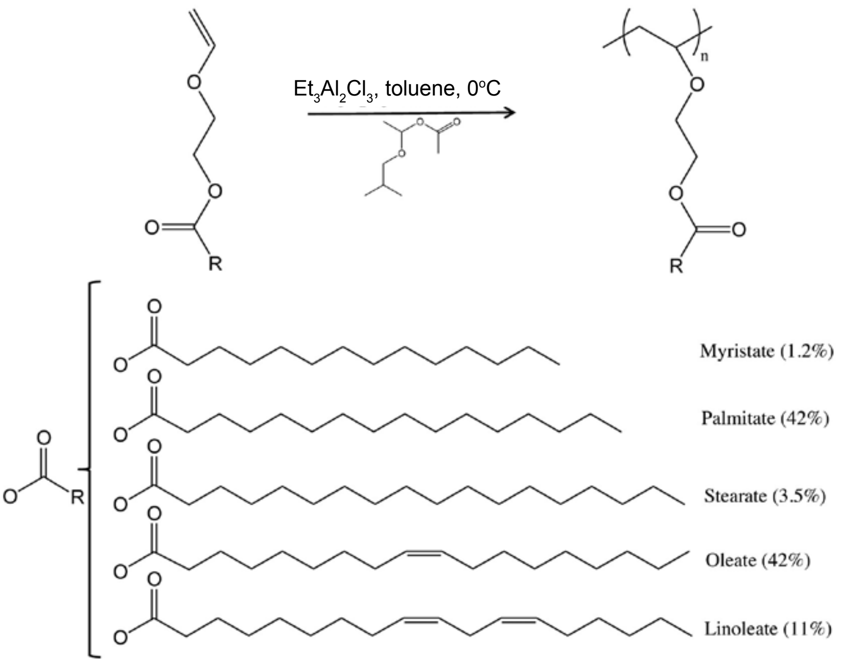

Figure 5. An illustration of the cationic polymerisation process used to produce poly(2-VOEP).

polymerisation was a 'living' polymerisation, the polymer produced possessed an average molecular weight relative to polystyrene standards of 16 000 g mole^{-1} and a molecular weight distribution of 1.15. The very narrow molecular weight distribution obtained suggests a living polymerisation, but further study is needed to confirm the obtainment of a living polymerisation. *Figure 6* provides the ^{1}H NMR spectrum of the poly(2-VOEP) sample produced from the study. A comparison of the ^{1}H NMR obtained for 2-VOEP (*Figure 3*) to that obtained for poly(2-VOEP) shows that internal double bonds associated with the parent PO were retained during the polymerisation, while the vinyl ether double bonds were consumed. While it has been previously demonstrated that the internal doubles associated with a plant oil can be polymerised using a cationic mechanism (Sharma *et al.*, 2010; Badrinarayanan *et al.*, 2009), the specific polymerisation system utilised for this study produced cationic species that were reactive enough to polymerise the more electron-rich vinyl ether double bonds, but not the less reactive internal double bonds. Peak integration of the methyl protons associated with fatty acid ester pendant groups to the protons associated with the internal doubles indicated that essentially none of the PO-based double bonds were consumed during the polymerisation.

Figure 7 provides a comparison of the thermal behaviour of poly(2-VOEP) to PO. The thermogram obtained for poly(2-VOEP) showed a clear melting endotherm with the peak at about 15°C. Thus, despite the decrease in molecular mobility associated with the attachment of the fatty acid ester groups to a polymer backbone, the long fatty acid alkyl chains were still able to undergo crystallisation. A comparison of the heat of fusion obtained for the parent PO (58 J g^{-1}) to that for poly(2-VOEP) (29 J g^{-1}) shows that the polymeric nature of poly(2-VOEP) does substantially reduce the extent of fatty acid ester alkyl group crystallisation. A glass transition (Tg) for poly(2-VOEP) was not observed from the DSC thermogram shown in *Figure 7*. This may simply be due to the temperature range used for the measurement. For an analogous vinyl ether polymer derived from SBO, *i.e.* poly(2-VOES), a Tg of -98°C was observed (Alam and Chisholm, 2011). Unfortunately, due to limitations of the DSC instrument, temperatures below about -80°C could not be reached for the characterisation of poly(2-VOEP).

Synthesis and Characterisation of the Polyol of Poly[2-(vinyloxy)ethyl palmitate]

The polyol of poly(2-VOEP) [HO-poly(2-VOEP)] was produced using a common route for the production of plant oil-based polyols. As shown in *Figure 8*, the double bonds present in the fatty acid ester pendant groups of poly(2-VOEP) were first epoxidised using peroxy acetic acid and then the epoxy groups were subsequently ring-opened with

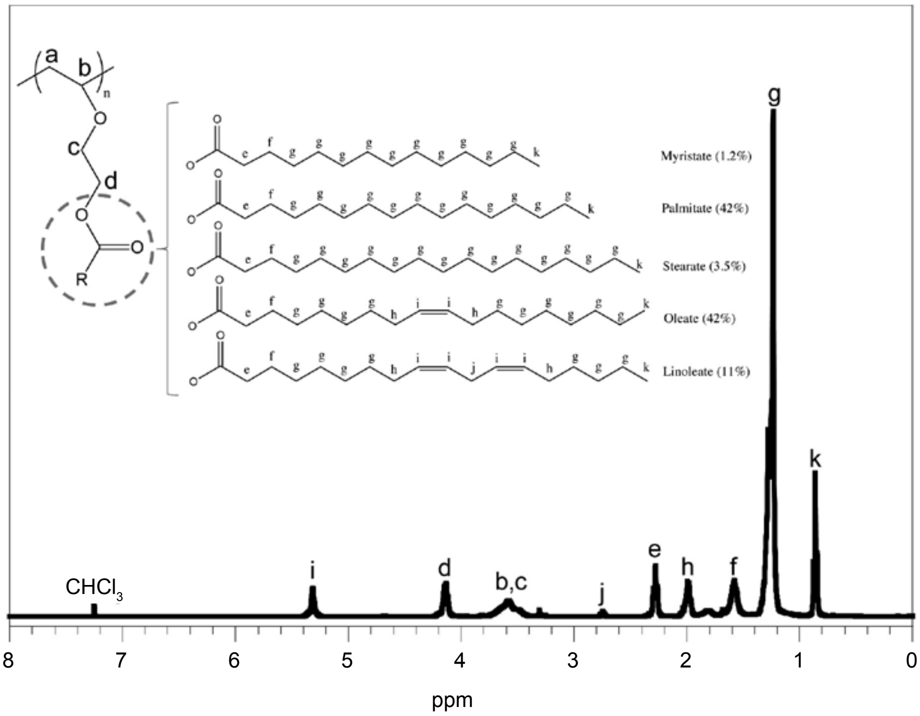

Figure 6. The ^{1}H NMR spectrum of the poly(2-VOEP) sample produced for the study.

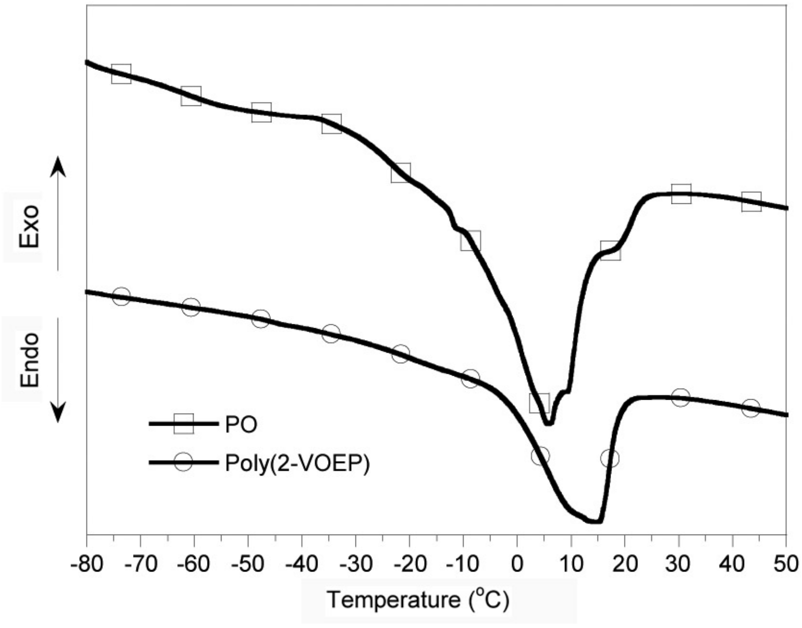

Figure 7. DSC thermograms for poly(2-VOEP) and palm oil. The thermograms represent the second heating cycle.

methanol. With this process, assuming essentially complete conversion of both the epoxidation step and the epoxy-ring opening step, each double bond is converted to a secondary hydroxyl group and a methoxy group. The synthetic process for the production of HO-poly(2-VOEP) was monitored using ^{1}H NMR. As shown in *Figure 9*, epoxidation of poly(2-VOEP) resulted in essentially complete disappearance of the vinyl protons (*a* in *Figure 9*) and the production of new protons associated with the epoxide functionality (*d* in *Figure 9*). These results confirm the successful synthesis of epoxidised poly(2-VOEP) [E-poly(2-VOEP)]. The reaction of E-poly(2-VOEP) with methanol resulted in essentially complete disappearance of the protons associated with the epoxide groups (*d* in *Figure 9*) and the appearance of new protons associated with the methoxy functionality derived from methanol (*e* in *Figure 9*). In addition, the methine proton on the carbon alpha to the methoxy group can be seen at

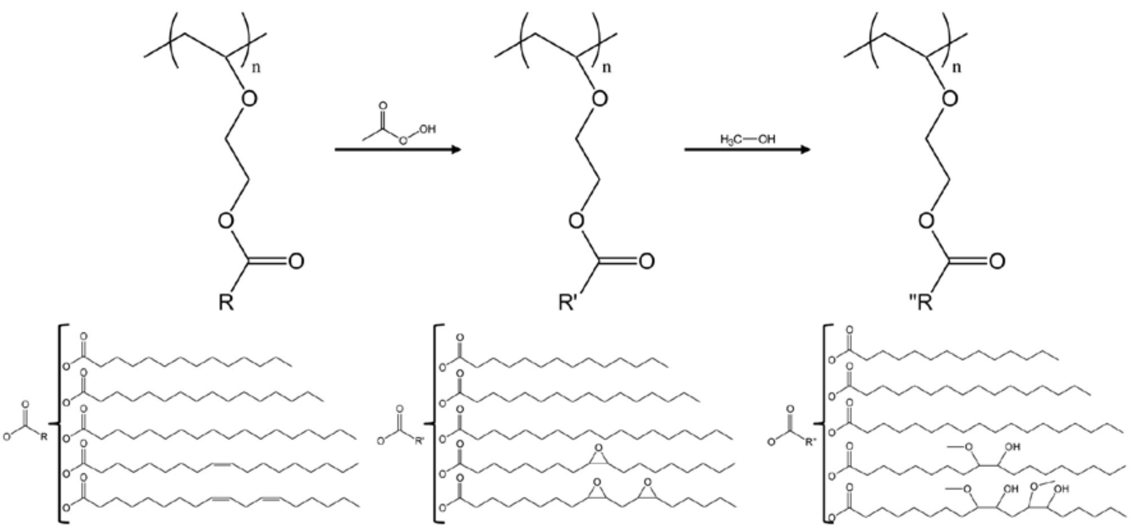

Figure 8. An illustration of the synthetic route used to produce HO-poly(2-VOEP) from poly(2-VOEP).

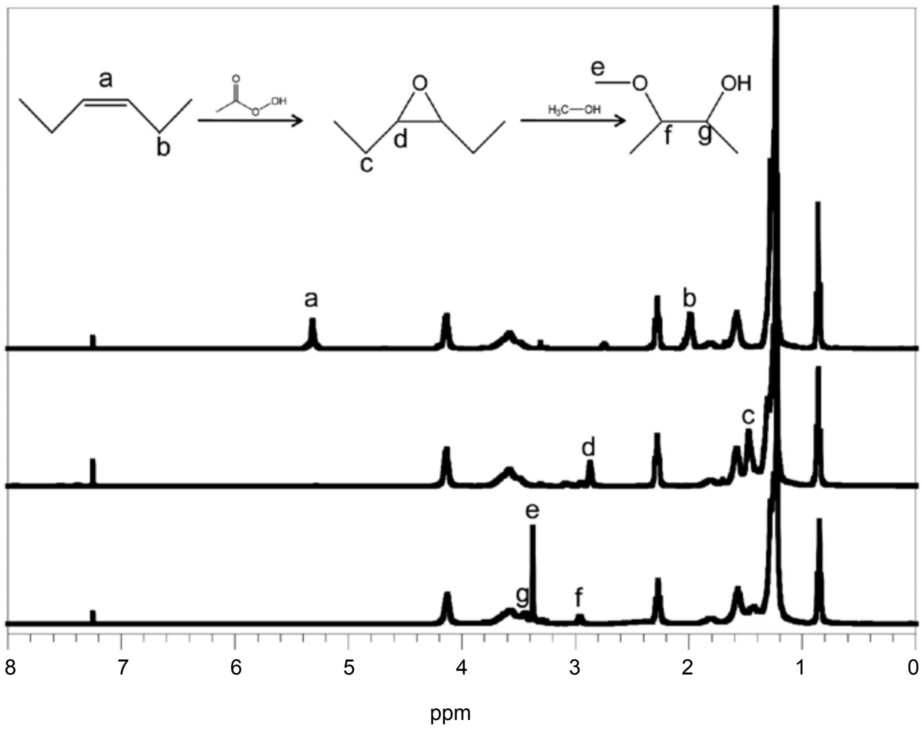

Figure 9. The ^1H NMR spectra illustrating the successful synthesis of HO-poly(2-VOEP) from poly(2-VOEP): poly(2-VOEP) (top); E-poly(2-VOEP) (middle); and HO-poly(2-VOEP) (bottom).

2.95 ppm (*f* in *Figure 9*). According to previous work by Moser and Erhan (2007) involving the synthesis of α-hydroxy ethers from 9,10-epoxystearates, the peak associated with the methine proton on the carbon attached to the hydroxyl group (*g* in *Figure 9*) as well as the hydroxyl proton should occur at approximately 3.6 to 3.8 ppm. Since this region of the spectrum for HO-poly(2-VOEP) also contains peaks associated with the protons derived from 2-HEVE (*b* and *c* in *Figure 6*), they were difficult to observe.

Figure 10 displays the FTIR spectra for poly(2-VOEP), E-poly(2-VOEP), and HO-poly(2-VOEP). With the exception of the broad band centred at about 3500 cm^{-1} for HO-poly(2-VOEP), all three spectra were similar. The broad band at 3500 cm^{-1} for HO-poly(2-VOEP) was due to the presence of the hydroxy functionality and confirms successful ring-opening of the epoxy groups of E-poly(2-VOEP) by methanol to produce the polyol. The other, more subtle, difference in the spectra can be observed at 3005 cm^{-1}. For the spectrum of poly(2-VOEP), a relatively weak band at 3005 cm^{-1} can be observed that is absent in the spectra for E-poly(2-VOEP) and HO-poly(2-VOEP). This band is due to the C-H stretch of the double bonds present in poly(2-VOEP).

The influence of the derivatisation steps on polymer thermal properties was characterised using DSC. As shown in *Figure 11*, the introduction of epoxy groups into the oleic and linoleic ester groups of poly(2-VOEP) did not significantly affect crystallisability, as indicated by the similar heats of fusion (ΔHm) and melting temperatures (Tm) obtained for poly(2-VOEP) (Tm = 15°C, ΔHm = 29 J g^{-1}) and E-poly(2-VOEP) (Tm = 16°C, ΔHm = 26 J g^{-1}). This result suggests that the crystallinity observed for poly(2-VOEP) is primarily due to crystallisation of the saturated fatty ester pendant chains. While no Tg was observed for poly(2-VOEP) over the temperature range used for the DSC measurements, a Tg at approximately -60°C was observed for E-poly(2-VOEP). This Tg is essentially the same as that obtained for epoxidised poly(2-VOES) (Alam, 2012). Ring-opening of the epoxy groups with methanol resulted in a further increase in Tg to approximately -43°C, no change in Tm, and slight increase in ΔHm to 32 J g^{-1}. The increase in Tg can be attributed to a reduction in polymer chain segmental mobility due to hydrogen bonding interactions involving the hydroxyl groups. The marginal increase in ΔHm may be due to more extensive phase separation between the hydroxy-functional pendant chains and the saturated pendant chains enabling a higher extent of crystallinity to be achieved for the latter.

Polyurethane Cure Kinetics

The HO-poly(2-VOEP) was used to produce polyurethane thermoset networks using HDT as the isocyanate-functional component. For comparison purposes, polyols were produced from PO and SBO to prepare analogous polyurethane networks. Due to the dramatic difference in the hydroxyl equivalent weight and the number of hydroxyl groups per molecule between HO-poly(2-VOEP), HO-PO, and HO-SBO, it was of interest to characterise the rate of the development of the crosslinked network. Although urethane formation from a hydroxyl-functional material and an isocyanate-functional

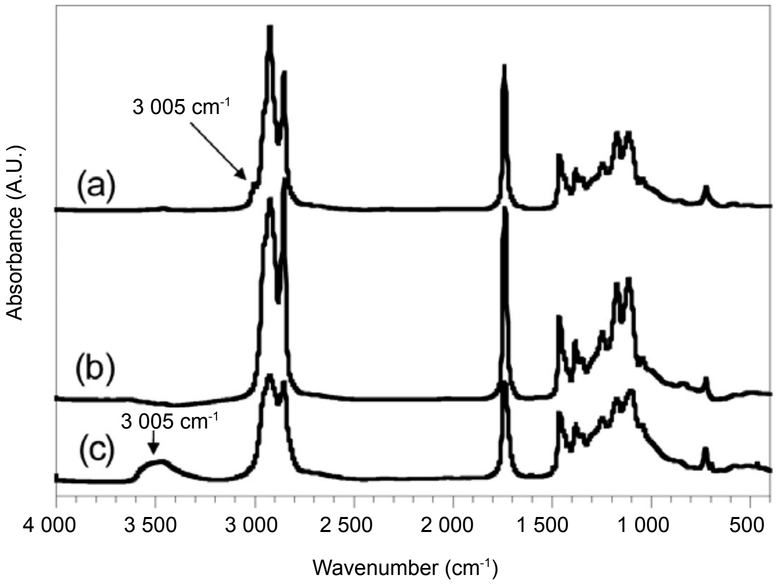

Figure 10. FTIR spectra illustrating the successful synthesis of HO-poly(2-VOEP) from poly(2-VOEP). (a) Poly(2-VOEP); (b) E-poly(2-VOEP); (c) HO-poly(2-VOEP).

material can occur at room temperature with the use of an appropriate catalyst, curing for the study was done at 100°C to ensure complete curing of all three urethanes of interest. Elevated temperature curing was also deemed important considering the fact that the hydroxyl groups involved in urethane formation are secondary hydroxyls, which are of lower reactivity than the primary hydroxyls typically associated with polyurethane materials.

As shown in *Figure 12*, the HO-PO/HDT mixture required approximately 18 min at 100°C for the material to start to increase in viscosity due to urethane formation and another 30 min or so was required for the complex viscosity to reach 10 000 Pa-s. In contrast, the complex viscosity for the HO-poly(2-VOEP)/HDT mixture started to increase after just 3 min and reached 10 000 Pa.s after an additional 9 min. For both the HO-PO/HDT mixture and the HO-poly(2-VOEP)/HDT mixture, the concentration of hydroxyl groups and isocyanate groups were similar; thus, the kinetics of urethane formation for both mixtures would have been similar. The much

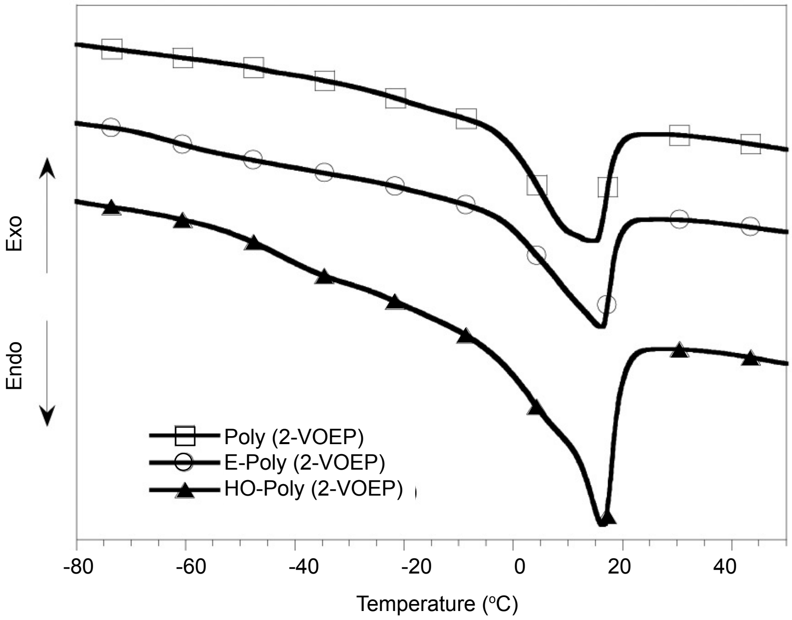

Figure 11. DSC thermograms illustrating the melting behaviour of poly(2-VOEP), E-poly(2-VOEP), and HO-poly(2-VOEP). The thermograms represent the second heating cycle.

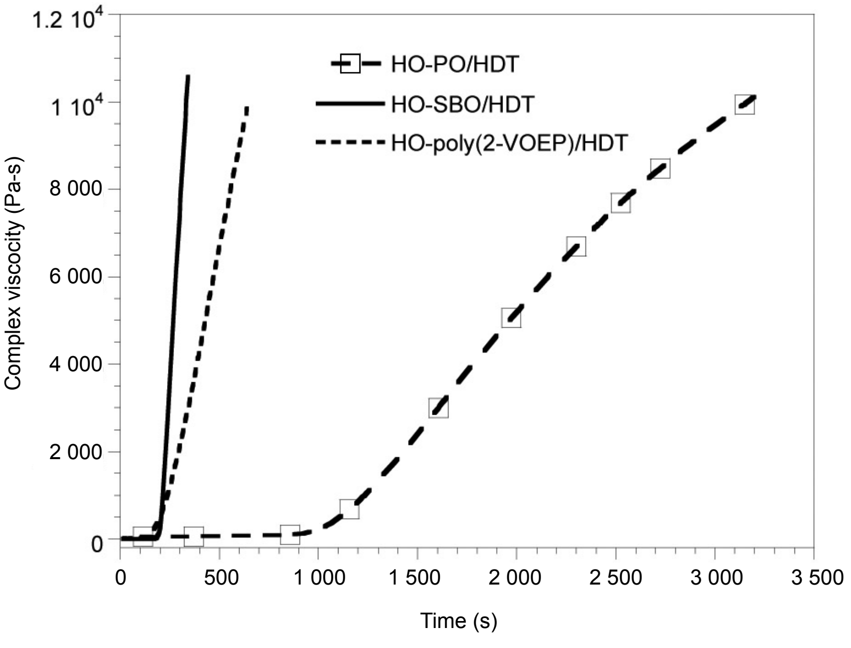

Figure 12. Complex viscosity as a function of time at 100°C.

faster increase in complex viscosity observed for the HO-poly(2-VOEP)/HDT material can be attributed to the dramatically higher number of hydroxy groups per molecule for HO-poly(2-VOEP), which translates to the gel-point being reached at much lower extents of conversion of hydroxy and isocyanate groups to urethane groups (Alam and Chisholm, 2011).

For the HO-SBO/HDT mixture, the concentration of hydroxyl groups and isocyanate groups is much higher than for either the HO-PO/HDT or HO-poly(2-VOEP)/HDT materials. As a result, the rate of urethane formation would be significantly faster. In addition, since the number of functional groups per molecule for both HO-SBO and HDT is 3 or higher, every reaction leading to the formation of a urethane group contributes to the crosslink density. Due to these factors, the crosslinked network for HO-SBO/HDT is developed faster than either of the two PO-based materials.

Polyurethane Thermoset Network Properties Based on Free Films

Free films were used to characterise mechanical and viscoelastic properties of the polyurethane networks of interest. *Figure 13* displays the DMA results obtained for the urethane networks. A comparison of the data for the HO-poly(2-VOEP)/HDT urethane to the HO-PO/HDT urethane shows that HO-poly(2-VOEP) enabled a slightly higher Tg, but a substantially higher crosslink density. Based on the peak of the tan δ curves, shown in *Figure 13*, the Tg for the HO-PO/HDT urethane was -5°C, while that for the HO-poly(2-VOEP) urethane was -2°C. The major difference in viscoelastic properties between these two urethane networks was the storage moduli at temperatures above the Tg. For thermoset networks, the storage moduli in this temperature region, typically referred to as the rubbery plateau region, is largely dependent on crosslink density. In fact, using the theory of rubbery elasticity, the crosslink density can be estimated from the following equation (Flory, 1953; Murayama, 1978):

$$\upsilon = E'/(3RT)$$

where υ is the crosslink density defined as the moles of crosslinks per unit volume of material, R is the gas constant, E′ is storage modulus in the rubbery plateau region, and T is the temperature corresponding to the storage modulus value (Hill, 1992). Using this relationship, the crosslink density for the HO-PO/HDT urethane network and the HO-poly(2-VOEP)/HDT network was 2.21×10^{-4} moles cm^{-3} and 9.06×10^{-4} moles cm^{-3} respectively. The higher crosslink density obtained with HO-poly(2-VOEP) can be largely attributed to the much higher number of hydroxyl groups per molecule compared to HO-PO. The average number of double bonds present in PO triglycerides is approximately 1.8 with 4.0%-10.5% possessing no unsaturation (*i.e.* trisaturated triglycerides) and 41%-59% being monounsaturated (*i.e.* disaturated-monounsaturated triglycerides). Assuming complete conversion of the double bonds present in PO to hydroxyl groups, the urethane network derived from HO-PO would contain about 4.0%-10.5% of completely saturated triglycerides, which do not contribute to the formation of the crosslinked network, and about 41%-59% of the HO-PO existing as basically dangling chains attached to the network, as illustrated in *Figure 14.* Although these monohydroxy-functional triglycerides get incorporated into the network during curing, they do not contribute to the crosslink density of the

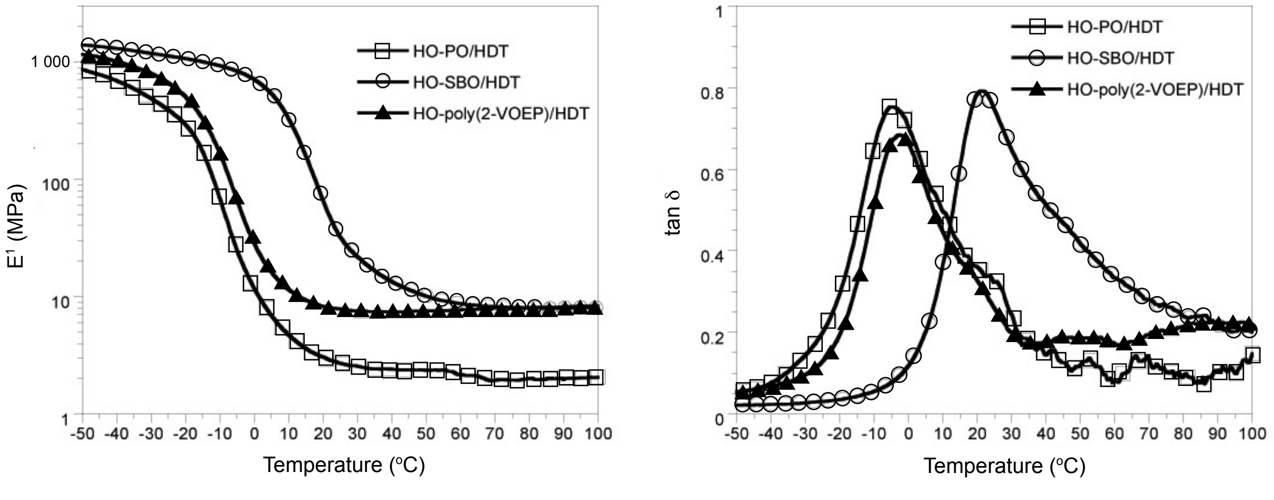

Figure 13. DMA results obtained for the three polyurethane networks of interest.

network. In contrast, due to the polymeric nature of poly(2-VOEP) each polymer molecule would be expected to possess at least two hydroxyl groups per molecule. For example, the poly(2-VOEP) sample used for the study was found to possess a number-average molecular weight of 16 000 g mole^{-1} relative to polystyrene standards. If the assumption is made that this molecular weight is close to the actual molecular weight, then the degree of polymerisation would be approximately 47. Since the percentage of monounsaturated and diunsaturated fatty acid esters in PO is about 40% and 10%, respectively, each polymer molecule, on average, should have approximately 38 hydroxyl groups. As a result, each polymer molecule contributes to the crosslink density of the urethane network.

It was somewhat surprising that the Tg of the HO-poly(2-VOEP)/HDT urethane network was not substantially higher than that of the HO-PO/HDT network. Typically, relatively high crosslink densities restrict segmental mobility resulting in an increase in Tg. However, despite the considerably higher crosslink density obtained with the use of HO-poly(2-VOEP), the network still contains a large number (*i.e.* approximately 50% on average) of dangling saturated fatty ester chains that most likely plasticise the network and perhaps minimise the restrictions in segmental mobility induced by the crosslinks.

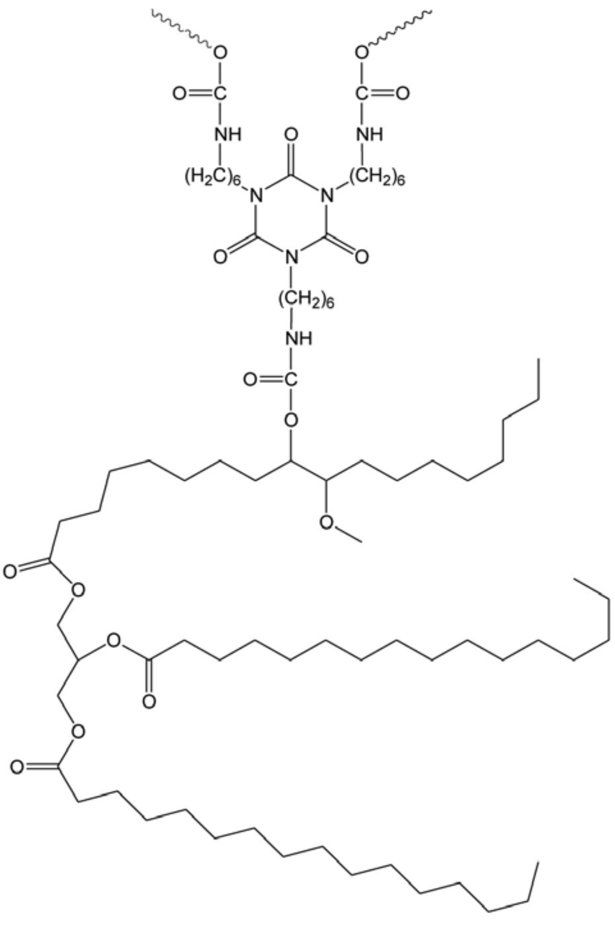

Figure 14. An illustration of dangling chain ends attached to the HO-PO/HDT network resulting from the presence of disaturated-monounsaturated triglycerides.

The urethane network based on HO-SBO (*i.e.* HO-SBO/HDT) was found to possess a much higher Tg than either the HO-PO/HDT or HO-poly(2-VOEP)/HDT networks. Compared to PO, SBO has much higher number of double bonds per triglyceride. On average, the number of double bonds per triglyceride for SBO is approximately 4.5. As a result, each HO-SBO molecule would be expected to contribute to the crosslink density of the HO-SBO urethane network. In addition, the percentage of saturated fatty esters in SBO is only about 15%. Thus, plasticisation of the network by dangling chains derived from saturated fatty esters is much less of a factor compared to networks derived from either HO-PO or HO-poly(2-VOEP). Both the relatively high crosslink density and the much lower level of saturated fatty ester dangling chains surely attribute to the higher Tg observed for the HO-SBO-based urethane network, but the most significant factor is most likely the higher level of urethane units incorporated into the HO-SBO/HDT network. Since the hydroxy equivalent weight of HO-SBO is much lower than that of HO-PO and HO-poly(2-VOEP), more than twice the amount of HDT was required to maintain and equivalent hydroxyl/isocyanate ratio of 1.0/1.1. The hydrogen bonding associated with the urethane linkages as well as the relatively rigid nature of the cyclic isocyanurate groups derived from HDT were most likely the most significant factors contributing to the higher Tg of the HO-SBO/HDT urethane network. It is interesting to note that, despite the much higher hydroxy equivalent weight of HO-poly(2-VOEP) compared to HO-SBO, the polymeric nature of HO-poly(2-VOEP) allowed for a polyurethane network that had essentially the same crosslink density as the HO-SBO-based network. Using the rubbery plateau modulus and Equation (I), the crosslink density for the HO-SBO-based urethane network was determined to be 8.78 x 10^{-4} moles cm^{-3}.

The thermal properties of the urethane networks were characterised using DSC. As shown in *Figure 15*, the urethane network based on HO-PO exhibited a weak endotherm with a peak temperature of -3°C. This endotherm indicates that, despite the presence of crosslinks, a small amount of crystallisation of the fatty ester side chains occurs. For the HO-poly(2-VOEP)/HDT network, a very slight endotherm was barely discernable at -5°C, indicating that the higher crosslink density obtained for this network largely inhibits side chain crystallisation. Due to the low level of saturated fatty ester side chains, the HO-SBO/HDT network showed no evidence

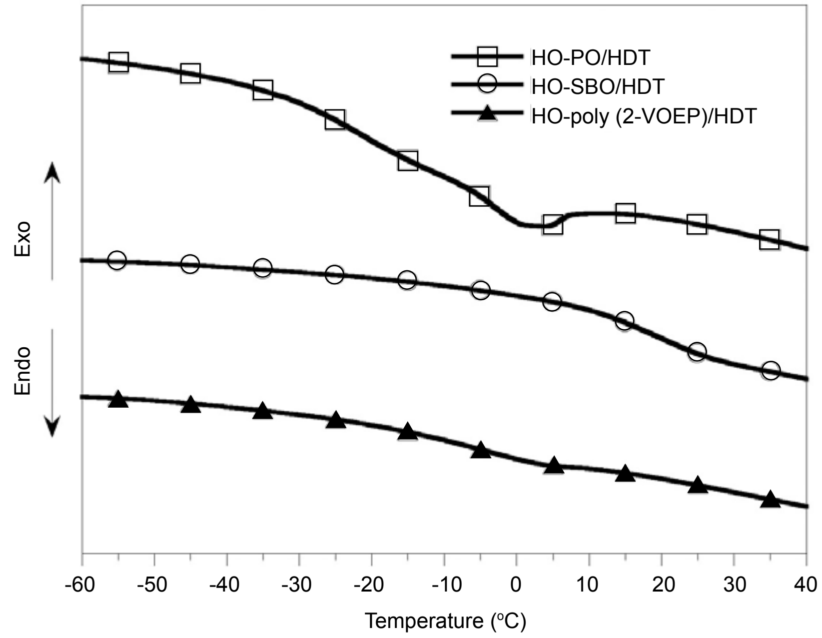

Figure 15. DSC thermograms for the polyurethane networks of interest. The thermograms represent the second heating cycle.

of a melting transition. A Tg for the HO-SBO/HDT network was observed at 20°C.

The gel content of the three urethane networks was determined using free-film specimens and Soxhlet extraction using toluene as the extracting medium. The extraction was carried out over a 4 hr period and the insoluble fraction (*i.e.* gel content) determined in duplicate. The gel content for the HO-PO/HDT, HO-SBO/HDT, and HO-poly(2-VOEP)/HDT urethane networks were 89, 90, and 93 weight percent, respectively. The relatively low gel content obtained with the HO-PO/HDT urethane is consistent with the relatively low crosslink density and the presence of saturated triglycerides. The higher gel content obtained with the HO-poly(2-VOEP)/HDT urethane as compared to both the HO-PO/HDT and HO-SBO/HDT networks can be attributed to the higher number of functional groups per molecule associated with HO-poly(2-VOEP), which allows the gel point to be reached at lower functional group conversion and ensures that the polymer molecules are incorporated into the network even if complete functional group conversion is not reached during curing. In addition, HO-poly(2-VOEP), unlike HO-PO, does not contain non-reactive fully saturated triglycerides.

The mechanical properties of the urethane networks were characterised using tensile testing, and the values for Young's modulus, tensile strength, and elongation at break are reported in *Table 3*. Representative stress – strain data are provided in *Figure 16*. The HO-PO/HDT network exhibited a relatively low Young's modulus and tensile strength representative of a soft pliable material. In comparison, the HO-poly(2-VOEP)/HDT urethane had a Young's modulus that was about four times higher. In addition, the tensile strength was higher and the elongation at break was lower. These results are consistent with the significantly higher crosslink density of the HO-poly(2-VOEP)/HDT urethane as compared to the HO-PO/HDT network. The HO-SBO/HDT network provided the highest Young's modulus, tensile strength, and elongation of all three urethanes. This result is consistent with the higher urethane functional group content for the HO-SBO/HDT material. It is well understood that urethane moieties impart significant toughness and strength to a material due to hydrogen bonding interactions.

Properties of Polyurethane Coatings

In addition to free films, coated substrates were produced and tested. The polyol/HDT blends were cast over substrates using a drawdown process and subsequently cured at 100°C. With the coated substrates, the solvent resistance, pendulum hardness, flexibility, and impact resistance was characterised. The data obtained is provided in *Table 4.*

As shown in *Table 4*, the thickness of all coatings produced were similar and in the range of 78 to 88 μm. The solvent resistance was found to be the highest for the HO-SBO/HDT coating and the lowest for the HO-PO/HDT coating. These results are consistent with the crosslink density and Tg data obtained from free films. The HO-SBO/HDT urethane network and the HO-poly(2-VOEP)/HDT urethane network were shown to possess a similar crosslink density that was substantially higher than that for the HO-PO/HDT urethane. Crosslinks inhibit swelling and diffusion of the solvent into the coating. Although the crosslink density for the HO-SBO/HDT network and the HO-poly(2-VOEP)/HDT network were similar, at ambient temperature, the HO-poly(VOEP)/HDT network is in the rubbery state, while the Tg for the HO-SBO-based network is very close to ambient temperature. Thus, diffusion of solvent molecules into the HO-poly(VOEP)/HDT coating would be expected to be easier due to the higher polymer chain segmental mobility at ambient temperature for this network. In addition, the higher urethane functional group content of HO-SBO/HDT would also be expected to enhance solvent resistance due to hydrogen bonding interactions. All coatings exhibited very good flexibility as indicated by the mandrel bend results. With regard to impact resistance, the HO-poly(VOEP)/HDT coating showed lower impact resistance than the other two urethane coatings, which was consistent with the tensile testing results that indicated that this material had the lowest ductility. Lower ductility and impact resistance were most likely due to the relatively high crosslink density and relatively low urethane functional group content of the HO-poly(VOEP)/HDT coating.

CONCLUSION

Overall, the results of the study clearly showed that converting PO triglycerides into a polymer

TABLE 3. RESULTS OBTAINED FROM TENSILE TESTING THE URETHANE NETWORKS OF INTEREST

Composition	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
HO-PO	3.2 ± 0.3	1.6 ± 0.2	63 ± 3
HO-SBO	17.8 ± 2.7	8.4 ± 1.2	83 ± 5
HO-poly(2-VOEP)	12.2 ± 0.4	2.9 ± 0.2	30 ± 2

TABLE 4. PROPERTIES OF POLYURETHANE COATINGS

Composition	HO-PO/HDT	HO-SBO/HDT	HO-poly(2-VOEP)/HDT
Thickness (μm)	83 ± 3	88 ± 4	78 ± 2
MEK double rubs	130 ± 8	230 ± 10	180 ± 8
Pendulum hardness (s)	20 ± 0	37 ± 0	62 ± 1
Mandrel bend test (%)	100	100	100
Reverse impact (ft.lb.)	≥ 172	≥ 172	120

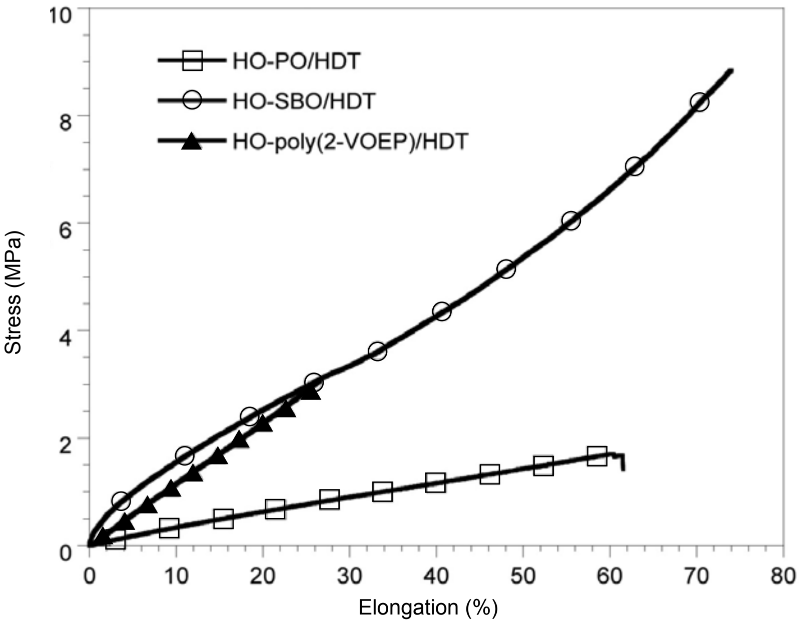

Figure 16. Stress – strain data obtained for the urethane networks of interest.

possessing PO-based fatty acid ester pendant groups provides significant advantages with respect to the production of thermoset networks. The urethane network derived from HO-poly(2-VOEP) cured much faster and had significantly higher modulus, tensile strength, hardness, chemical resistance, and gel content compared to the analogous urethane network derived from HO-PO. These properties enhancements can all be attributed to the dramatically higher number of hydroxyl groups per molecular for HO-poly(2-VOEP) as compared to HO-PO. For the HO-poly(2-VOEP) material used for the study, it was estimated that the number of hydroxyl groups per polymer molecule, on average, may be as high as 38, while the average number of hydroxyl groups per molecule for the HO-PO sample was, at maximum, 1.8. This dramatically higher number of hydroxyl groups per molecule for HO-poly(2-VOEP) results in the gel-point of the urethane network being reached at much lower functional group conversion and provides much higher crosslink density of cured urethanes.

Due to the much higher number of functional groups per triglyceride associated with SBO, this plant oil has been used extensively for the production of thermoset materials. The results of the study showed that, despite the much lower hydroxyl equivalent weight of HO-poly(2-VOEP) as compared to HO-SBO, the much higher number of hydroxyl groups per molecule associated with HO-poly(2-VOEP) enabled a polyurethane that was more similar in properties to the HO-SBO-based urethane than the HO-PO-based urethane.

ACKNOWLEDGEMENT

The authors thank the United States Department of Agriculture/National Institute of Food Agriculture (grant 2012-38202-19283) and the Department of Energy (DE-FG36-08GO088160) grant for financial support as well as the MPOB for supplying palm oil.

DISCLAIMER

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