

**Original citation:**

Clark, Andrew J. and Hoong, Seng Soi. (2014) Copolymers of tetrahydrofuran and epoxidized vegetable oils : application to elastomeric polyurethanes. *Polymer Chemistry*, 5 (9). pp. 3238-3244.

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# Copolymers of Tetrahydrofuran and Epoxidized Vegetable Oils: Application to Elastomeric Polyurethanes

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5 Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

The Lewis Acid ring-opening of epoxidized vegetable oils (EVO's) in the presence of tetrahydrofuran (THF) gives rise to polyether polyol co-polymers p(THF-*stat*-EVO). The effect of Lewis acid, vegetable oil substrate (epoxidised methylolate EMO, epoxidised cocoa butter ECB, and epoxidised palm oil EPO) and conditions (concentration, temperature and time) on the molecular weight, polydispersity, hydroxyl value and thermal properties of the p(THF-*stat*-EVO) macromonomers was determined. Elastomeric polyurethanes were prepared from p(THF-*stat*-EVO) macromonomers and MDI and their mechanical and thermal properties determined. The properties of the polyurethane derived from p(THF-EPO) were compared to that derived from the homopolymer of epoxidised palm oil (EPO) prepared by Lewis acid ring-opening in the absence of THF. The co-polymer incorporating THF gave rise to a material with significantly greater tensile strength [p(THF-EPO-MDI) = 9.1 MPa, p(EPO-MDI) = 1.5 MPa] and elongation at break [p(THF-EPO-MDI) = 425%, p(EPO-MDI) = 70%] with little compromise on thermal stability [p(THF-EPO-MDI)  $T_{\text{decomp}10\%}$  = 378 °C,  $T_{\text{decomp}50\%}$  = 414 °C, p(EPO-MDI)  $T_{\text{decomp}10\%}$  = 379 °C  $T_{\text{decomp}50\%}$  = 424 °C].

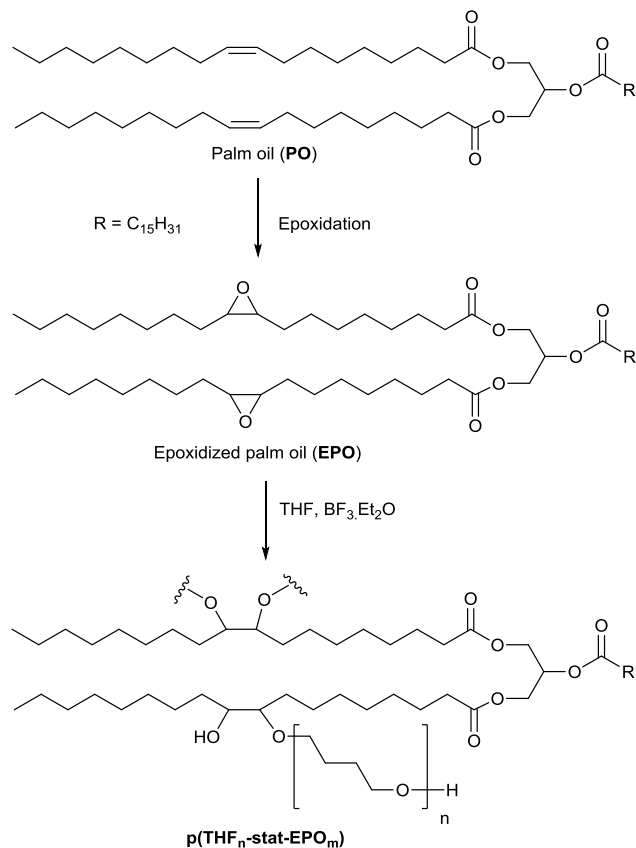
## 20 Introduction

Vegetable oils are important renewable platform chemicals.<sup>1,2</sup> In particular, the ability to easily chemically modify vegetable oils has made them attractive feedstocks for the polymer industry.<sup>3-5</sup> Vegetable oil triglycerides are complicated structures containing statistical mixtures of different fatty acid components. For example the palm oil triglyceride (PO) used in this study contained six different fatty acid chains [saturated: 42% palmitic (16:0), 3.8% stearic (18:0), 0.4% arachidic (20:0) unsaturated: 43.4% oleic (18:1), 10.0% linoleic (18:1) and 0.4% linolenic (18:3)]<sup>6</sup> with 1.9 alkene groups per molecule on average, (Fig. 1). Vegetable oils can be functionalized by reactions at the ester group (transesterification<sup>7,8</sup> or transamidation<sup>9,10</sup>) or the alkene functionality.<sup>2</sup> The most common approach to functionalization is at the alkene group (normally via epoxidation<sup>11,12</sup> and ring opening reactions<sup>2</sup>) but hydroformylation,<sup>13,14</sup> ozonolysis,<sup>15,16</sup> metathesis<sup>17-22</sup> and thiol-ene<sup>23,24</sup> pathways have also been explored. Ring-opening of epoxidized vegetable oils (EVO's) with a range of nucleophiles furnishes secondary alcohol polyols which can be used to make polyurethanes.<sup>5, 25-29</sup> These secondary alcohols can also be used to ring-open ethylene oxide to give polyols with primary hydroxyl functionality which are more reactive to polyurethane formation.<sup>30</sup> An alternative approach to furnish primary polyols from vegetable oils utilizes ring-opening of epoxides with 1,3-propanediol.<sup>31</sup> Ionic-coordinative ring-opening polymerization<sup>32</sup> of epoxidized methylolate (EMO) followed by LiAlH<sub>4</sub> reduction to give polyether polyols with molecular weights ranging between 0.9-7 KDa can also be used

to make polyurethanes.<sup>33</sup> Polyol formation by ring-opening polymerization of epoxidised methylolate (EMO) and epoxidized soybean oil (ESO) have been studied using HSBF<sub>6</sub> and BF<sub>3</sub>·OEt<sub>2</sub> in dichloromethane respectively.<sup>34,35</sup> Polyether polyols derived from ESO exhibited thermally stable (>340 °C) highly cross-linked structures with glass transition temperatures between -16 and -48 °C.<sup>35</sup> After hydrolysis these cross-linked structures could be converted into hydrogels. Polyols (900-1200 g/mol) derived from HSBF<sub>6</sub> mediated ring-opening of EMO were reacted with 4,4'-methylene diphenyldiisocyanate (MDI) to make hard polyurethane rubbers,<sup>34</sup> while reaction with larger polyols (~7000 g/mol) furnished more flexible materials.<sup>32</sup> Tetrahydrofuran (THF) is a relatively cheap industrial solvent that can be prepared from agricultural waste via succinic acid and is therefore potentially renewable.<sup>36</sup> Polytetrahydrofuran, p(THF), is obtained from homopolymerization of THF through cationic polymerization catalyzed by strong Lewis acids (BF<sub>3</sub>, SbF<sub>5</sub>) or strong Bronsted acids (FSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>2</sub>OSO<sub>2</sub>CF<sub>3</sub>).<sup>37</sup> One use of the p(THF) is to make elastomeric polyurethanes. The ring strain of THF (5.63 kcal/mol) is smaller than the ring strain of alkylene oxides (27.28 kcal/mol)<sup>38</sup> but is high enough for ring opening polymerization. The cationic ring opening of THF can also be conducted in the presence of epoxides such as ethylene oxide (EO) and propylene oxide (PO) to generate copolymers of p(THF-EO) and p(THF-PO) respectively, which have molecular weights in the range of 3-5 KDa. This copolymerization of THF with EO or PO is usually initiated by diols such as 1,4-butanediol.<sup>39-41</sup> One advantage of copolymerizing THF with EO

or PO is the higher yield of polymers achievable (85-90%) compared to homopolymerization alone.<sup>42</sup> Other advantages included better elastomeric properties of polyurethanes (elongation, tensile strength and modulus) compared to PU elastomers derived from PO homopolymers or PO-EO copolymers.<sup>43</sup>

**Fig. 1.** Synthetic pathway for the preparation of polyols from palm oil.



We hypothesized that if epoxidized vegetable oils (EVO's) underwent Lewis acid mediated ring-opening polymerisation in THF, then the renewable co-polymers, p(THF-EVO) prepared, Figure 1, would have significantly different properties to those polyols derived from Lewis acid ring-opening of EVO's alone p(EVO). In addition, the p(THF-EVO) macromonomers would contain primary alcohol functionality making them more reactive with diisocyanates that would lead to highly elastomeric PU's. In this paper we report the Lewis acid catalyzed ring-opening of epoxidised methyloleate, cocoa butter and palm oils in the presence and absence of THF and compare the properties of PU's derived from them.

## Results and Discussion

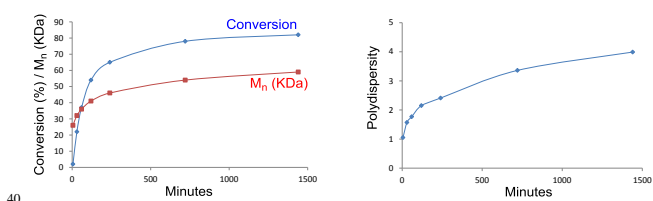
It has been reported that THF can be co-polymerized with ethylene oxide (EO) or propylene oxide (PO) with Lewis acids (BF<sub>3</sub>.OEt<sub>2</sub>, AlCl<sub>3</sub>, SnCl<sub>4</sub>)<sup>37</sup> or superacids (HBF<sub>4</sub>, ClSO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H).<sup>44</sup> In addition to these catalysts we screened FeCl<sub>3</sub>, AlCl<sub>3</sub>, TiCl<sub>4</sub>, CF<sub>3</sub>CO<sub>2</sub>H and H<sub>2</sub>SO<sub>4</sub> in the copolymerisation of epoxidized palm oil (EPO)<sup>45</sup> with THF at 20 °C with a 20:1 ratio of THF:EPO (w/w) over 24 h.<sup>†</sup>

**Table 1.** Screening of Lewis Acids as potential catalysts in the reaction of EPO with THF to give p(THF-*stat*-EPO).<sup>†</sup>

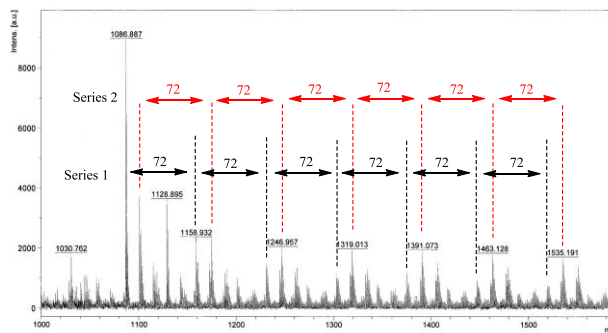
Entry <sup>a</sup>	Lewis Acid	Catalyst (mol %)	Conversion <sup>b</sup> (%) <sup>c</sup>	M <sub>n</sub> (KDa)	PDI
1	FeCl <sub>3</sub>	10.0	90 (60)	17	2.6
2	SnCl <sub>4</sub>	10.0	93 (77)	25	4.4
3	CF <sub>3</sub> SO <sub>3</sub> H	10.0	92 (79)	36	4.6
4	HBF <sub>4</sub>	2.0 <sup>d</sup>	95 (74)	22	3.8
5	BF <sub>3</sub> .Et <sub>2</sub> O	2.0 <sup>d</sup>	97 (88)	56	6.5
6	BF <sub>3</sub> .Et <sub>2</sub> O	1.0	80 <sup>e</sup>	45	3.2
7	BF <sub>3</sub> .Et <sub>2</sub> O	0.5	0	-	-
8	BF <sub>3</sub> .Et <sub>2</sub> O	2.5	gelled	-	-

<sup>a</sup> 20:1 THF:EPO (w/w) was used. <sup>b</sup> Percentage determined from GPC. <sup>c</sup> Weight % of THF in polymer in brackets. <sup>d</sup> Reaction mixtures gelled if 10 mol% was used. <sup>e</sup> Weight % of THF in polymer not determined.

**Fig. 2.** M<sub>n</sub>, conversion and PDI verses time for copolymerization of THF and EPO (20:1 w/w) with 1 mol% BF<sub>3</sub>.Et<sub>2</sub>O over 24 h.



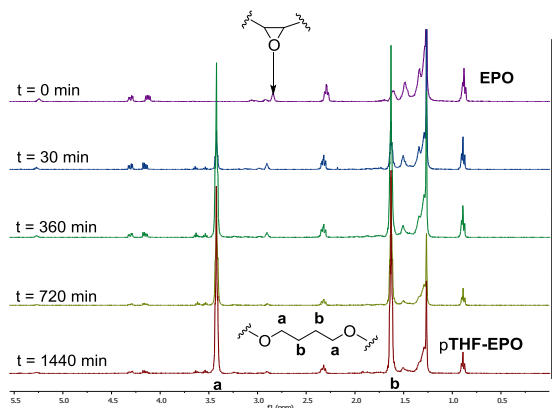
**Fig. 3.** MALDI-TOF of p(THF-EPO) showing repeating unit of 72Da.<sup>†</sup>



Mixtures were analysed by GPC. Only 5 catalysts showed activity in the ring-opening process, (entries 1-5), Table 1. Both HBF<sub>4</sub> (entry 4) and BF<sub>3</sub>.OEt<sub>2</sub> (entry 5) showed conversions at acceptable catalyst loadings (2 mol%). None of the catalysts studied caused homopolymerization of THF. Due to the high expense and toxicity of HBF<sub>4</sub> we chose BF<sub>3</sub>.OEt<sub>2</sub> for further study. Decreasing the amount of catalyst to 1 mol% slowed the reaction and lowered the degree of polymerization and cross-linking (entry 6), while increasing the amount of catalyst past 2.5 mol% led to gelling (entry 8), indicating that higher loadings generate more active polymer chains that promote cross-linking during polymerization. Copolymers were analysed by both MALDI-TOF-MS,<sup>†</sup> (Figure 3) and 400 MHz <sup>1</sup>H NMR<sup>†</sup> (Figure 4) to confirm incorporation of THF into the products. The change in % conversion, M<sub>n</sub> and PDI were determined over time under the conditions shown for entry 6, Table 1 (Figure 2). The significant increase in PDI as a function of time confirms that significant

cross-linking takes place at high conversion. Termination of the ring-opening polymerization can occur via hydrolysis (OH end group), or by elimination / cyclisation ( $-H_2O$ ). This coupled with the fact the **EPO** used in this study contained both C16 (42%) and C18 (58%) fatty acid chains which themselves could contain between (0-3 epoxides) leads to the observation of five series of different polymer families each with a repeating unit of 72 Da, Figure 3. For example series 1 shows a major peak at 1086.8 Da, which corresponds to the sodium adduct of p(THF<sub>2</sub>-stat-EPO) where the EPO has three C18 derived fatty acids but only 1 initial epoxide group. The rest of series 1 corresponds to further additions of THF to this parent peak. The series 2 peak at 1246.9 corresponds to p(THF<sub>4</sub>-stat-EPO) where the EPO had three C18 derived fatty acids but 2 initial epoxide groups. Analysis of the <sup>1</sup>H NMR clearly shows the decrease in epoxide peaks at 2.80-3.10 ppm and the growth of the peaks corresponding to incorporation of THF monomer units at 3.45-3.32 and 1.68-1.52 ppm. Attempts to use commercially available renewable solvent 2-Me-THF failed to lead to any polymerization.

**Fig. 4.** 400 MHz <sup>1</sup>H NMR of p(THF-EPO) versus time. †



We next investigated two control homopolymerizations, that of THF with itself and **EPO** with itself, (Table 2). We replaced THF with hexane (entry 1) which led to the homopolymerization of **EPO** (0.38M in hexane, no THF added) to give polymers with very much broader PDI's (17.3) due to cross-linking of the epoxides. MALDI-TOF-MS showed the repeating unit of the triglyceride functionality but also indicated the loss of one fatty acid side-chain. Decreasing the concentration of **EPO** in hexane (0.19M, entry 3) but keeping the other parameters the same resulted in smaller homopolymers with lower PDI's as expected. Increasing the temperature (20 → 60 °C) also led to lower molecular weight polymers with lower PDI's presumably due to more efficient chain termination during oligomerization at the higher temperature (entry 2). The same observations were made for the copolymerization of **EPO** with THF (entries 3-4). Decreasing the relative amount of THF:**EPO** led to gelling (compare Table 1, entry 6, with Table 2, entry 4) while increasing the temperature suppressed gelling (compare Table 1, entry 6 with Table 2 entry 5). This is likely due to the higher activation energy for THF ring-opening (51.3 kcal/mol) compared to epoxide ring-opening (20 kcal/mol).<sup>46</sup> We also prepared p(THF)

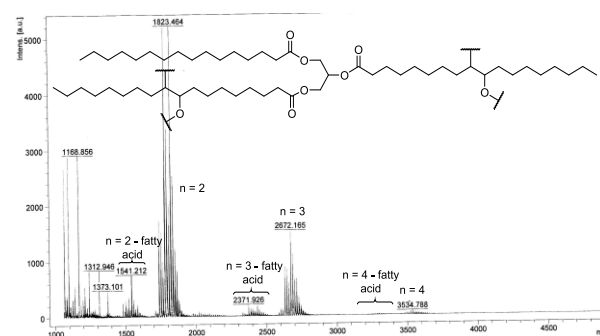
by the method of Dorai<sup>47</sup> as a benchmark for our study on PU's.

**Table 2.** Effect of concentration and temperature on homo- and copolymerization of **EPO** with and without THF.

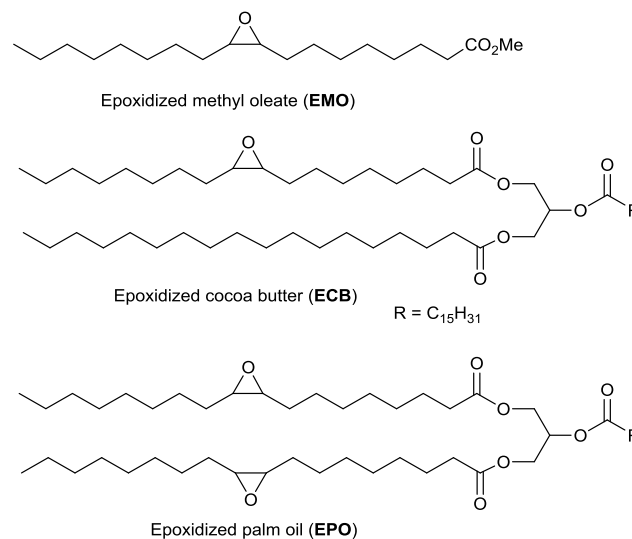
Entry	Conc (M)	Temp (°C)	Solvent	BF <sub>3</sub> .Et <sub>2</sub> O (mol %)	Conver. (%) <sup>a</sup>	M <sub>n</sub> (KDa)	PDI
1	0.38	20	hexane	3.5	90	27	17.3
2	0.38	60	hexane	3.5	83	17	3.6
3	0.19	20	hexane	3.5	85	16	3.1
4	0.06	20	THF	1.0	Gelled	-	-
5	0.09	60	THF	2.5	80	16	3.9

<sup>a</sup>Percentage determined from GPC.

**Fig. 5.** MALDI-TOF-MS for the homopolymerisation of **EPO**<sup>48</sup>.



**Fig. 6.** Epoxidized triglycerides used as monomers in this study.



We next investigated the copolymerization of THF with EMO, and ECB under a variety of conditions, Table 3. Previous studies have reported the ring-opening polymerisation of EMO under a variety of conditions in bulk, hexane or CH<sub>2</sub>Cl<sub>2</sub>.<sup>32-34</sup> All of these studies have used relatively high purity EMO to simplify characterisation. We chose to use a low commercial grade of EMO (77% purity) due to its low cost. This grade contains significant amounts of C16 fatty acids (12.5%). Much concern has been expressed about the use of food crops (e.g. palm oil, soyabean oil) for biofuels and bioplastics manufacture;

consequently we also examined the chemistry of epoxidized cocoa butter (a waste product from the confectionary industry) in addition to commercially available **EPO**.

For any specific oil, increasing the amount of catalyst led to higher molecular weights (compare entries 1/2, and 3/4, Table 3) and increasing the THF:**EVO** ratio retarded gelling. The acid and OH values were measured for the co-polymers obtained (entries 1, 4 and 7) as well as the homopolymer of EPO to determine appropriate ratios for PU formation with MDI, (Table 4). The larger acid value for the p(THF-EMO) derivative should be noted and indicates that a degree of hydrolysis of the methyl ester occurs under the reaction conditions.

**Table 3.** Effect of different vegetable oils on p(THF-EVO).

Entry	EVO	BF <sub>3</sub> .Et <sub>2</sub> O (mol %)	THF:EVO	Conver. (%)	M <sub>n</sub> (KDa)	PDI
1	<b>EMO</b>	2.5	20:1	75	8K	2.2
2	<b>EMO</b>	5.0	20:1	97	26K	2.1
3	<b>ECB</b>	5.0	20:1	82	16K	2.3
4	<b>ECB</b>	10.0	20:1	93	30K	2.8
5	<b>EPO</b>	2.0	12:1	Gelled	-	-
6	<b>EPO</b>	2.0	16:1	79	45K	3.2
7	<b>EPO</b>	2.0	24:1	83	56K	3.0

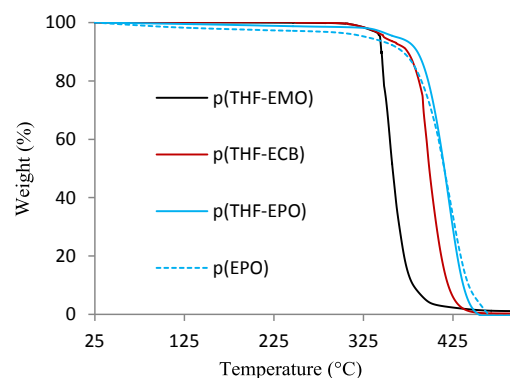
**Table 4.** Hydroxyl and acid values of p(THF-EVO).

Entry	Polymer	OH value <sup>a</sup> (mg KOH/g)	Acid value <sup>a</sup> (mg KOH/g)	M <sub>n</sub> (KDa)	PDI	T <sub>10%</sub> <sup>b</sup> (°C)
1	<b>P(THF-EMO)</b>	25	7	26K	2.1	345
2	<b>P(THF-ECB)</b>	27	1	30K	2.8	374
3	<b>P(THF-EPO)</b>	40	1	56K	3.0	386
4	<b>P(EPO)</b>	38	1	16K	3.1	371

<sup>a</sup>Determined using The American Oil Chemical Society official protocols, acid value (Te 1a-064), hydroxyl value Cd I3-60(89)<sup>49</sup>. <sup>b</sup>Temperature for 50% weight loss.<sup>‡</sup>

The thermal properties for the co-polymers were also obtained (Figure 7). The thermal stability of all three p(THF-EVO) polyols is greater than for conventional p(THF), or p(THF-PO) alone.<sup>41</sup> The T<sub>50%</sub> decomposition values for p(THF) = 330°C, p(THF-PO) = 280°C, compared to p(THF-EMO) = 358°C, p(THF-ECB) = 399°C, p(THF-EPO) = 416°C highlights the effect of increased cross-linking within these polyols.<sup>41</sup> The major decomposition mode for the p(THF-EVO)'s is likely to be due to THF depolymerisation.<sup>41</sup> As expected the thermal stability significantly increases for the triglyceride derivatives compared to p(THF-EMO), Table 4. A slight increase in T<sub>10%</sub> also occurs in the p(THF-EVO) series with increasing M<sub>n</sub> and PDI's [T<sub>10%</sub> p(THF-EMO) = 345°C, p(THF-ECB) = 374°C, p(THF-EPO) = 386°C]. The incorporation of the THF group into the polyol provides a degree of stability at lower temperature (compare T<sub>10%</sub> p(THF-EPO) = 386°C with p(EPO) = 371°C).

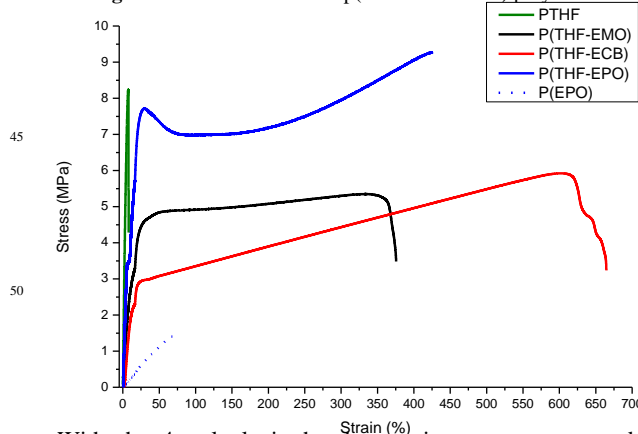
**Fig.7.** TGA of p(THF-EVO) polymers<sup>‡</sup>



**Table 5.** Properties of PU samples made from p(THF), p(THF-EVO) and p(EVO)<sup>‡</sup>

Entry	Polymer	Tensile strength (MPa)	Elongation at break (%)	Cross-link density x 10 <sup>-4</sup> (mol/cm <sup>3</sup> )
1	<b>P(THF-MDI)</b>	8.3	6	0.7
2	<b>P(THF-EMO-MDI)</b>	5.3	350	3.2
3	<b>P(THF-ECB-MDI)</b>	5.9	610	3.4
4	<b>P(THF-EPO-MDI)</b>	9.1	425	5.3
5	<b>P(EPO-MDI)</b>	1.5	70	2.0

**Fig.8.** Stress-strain curves of p(THF-EVO-MDI) polymers.<sup>‡</sup>



With the 4 polyols in hand, attention was now turned to preparing polyurethanes using 4,4'-methylenebis(phenyl isocyanate) (MDI). The ratio between the isocyanate group (NCO) and the hydroxyl group (OH) was kept between 1.02-1.05 to 1 in order to ensure that all the hydroxyl groups of copolymers were fully reacted and the PU samples were fully cured when the excess isocyanate group reacted with moisture from the air. Thermal analysis (TGA and DSC) were undertaken of the PU's as well as tensile testing in order to gain a better understanding of



their properties and strength. Figure 8 shows the stress-strain curves. Furthermore, swelling tests were conducted in order to determine the cross-linking density of the p(THF-EVO-MDI) samples by using the Flory-Rehner equation.<sup>50</sup>

Thermal analysis was carried out on the three novel p(THF-EVO-MDI) polymers and comparison made between p(EPO-MDI), Figures 9 and 10. Differential scanning calorimetry (DSC) analysis shows similar  $T_g$  values for the three THF derived polymers p(THF-EMO-MDI) = -71 °C, p(THF-ECB-MDI) = -75 °C, p(THF-EPO-MDI) = -76 °C which were lower than for the p(EPO-MDI) polymer (-49 °C) due to THF incorporation. This is in line with the known  $T_g$  value of -84 °C for p(THF) itself and reflects the high weight percent of ring-opened THF chains in the p\*THF-EVO's). Polyurethanes generally exhibit poor thermal stability, due to decomposition of the urethane linkage around 200 °C.<sup>25,29,52</sup> Vegetable oil derived polyurethanes normally show two-step degradation.<sup>52</sup> The first small step is degradation of the urethane bond to give primary amines and alkenes, isocyanates or alcohols or secondary amines<sup>33,53</sup> followed by the main loss of weight above 350 °C due to polyether chain scission.<sup>52</sup> The initial degradation is greatest for the p(THF-EMO-MDI) derivative due to the larger weight percentage of urethane linkages present within the polymer. Otherwise the degradation profiles are similar to others recorded for vegetable oil derived polyurethanes.<sup>52</sup> The thermal stability of both palm oil derived materials was similar [p(THF-EPO-MDI)  $T_{10\%}$  = 378 °C,  $T_{50\%}$  = 414 °C, p(EPO-MDI)  $T_{10\%}$  = 379 °C  $T_{50\%}$  = 424 °C], however the tensile properties were considerably different. Tensile strengths of all the p(THF-EVO)'s were in the range 5.3-9.1 MPa with elongations at break ranging from 350-610%. Three factors a likely to affect these values, the degree of cross-linking, the number of dangling chains and the  $T_g$  of the samples. The p(THF-MDI), Table 5 entry 1, control polymer shows relatively high tensile strength (8.3 MPa) but low elongation (6%).<sup>51</sup> Both the polymers derived from methylolate and cocoa butter, p(THF-EMO-MDI), entry 2, and p(THF-ECB-MDI), entry 3, were derived from oils with one epoxide group and the hydroxyl values of both macromonomers p(THF-EMO) and p(THF-ECB) were lower (25 and 27 mg KOH/g) than for that derived from palm oil p(THF-EPO). Therefore, the cross-link densities exhibited by the methylolate and cocoa butter derived polymers, p(THF-EMO-MDI), entry 2, and p(THF-ECB-MDI), were relatively low ( $3.2-3.4 \times 10^{-4}$  mol/cm<sup>3</sup>) compared to that derived from palm oil, p(THF-EPO-MDI),  $5.3 \times 10^{-4}$  mol/cm<sup>3</sup>. This relatively low cross-link density translated to a lower tensile strength, in the region of 5.3 MPa to 5.9 MPa, compared to 9.1 MPa for p(THF-EPO-MDI). However, there is a significant difference in elongation at break for the two polymers derived from methylolate and cocoa butter with p(THF-ECB-MDI), entry 3, significantly higher than for methylolate p(THF-EMO-MDI). This increased performance can be attributed to the increased plasticizing effect from the extra pendant saturated fatty acid chains found in p(THF-ECB-MDI). In comparison, p(THF-EPO-MDI) derived from palm oil, Table 5 entry 4, had a higher cross-link density and tensile strength exhibited but lower elongation at break as expected. Comparing the properties of the two palm oil derived polyurethanes, p(THF-EPO-MDI), entry 4, and p(EPO-MDI), entry 5, highlights the importance of how the original

macromonomer was prepared.  $\text{BF}_3 \cdot \text{OEt}_2$  mediated ring-opening polymerization of EPO in hexane to give macromonomer ultimately leads to a MDI-polyurethane polymer with 6 times less tensile strength and elongation at break compared to one prepared by ring-opening in THF due to the absence of the polymeric THF chains.

Fig.9. TGA of p(THF-EVO-MDI) polymers<sup>‡</sup>

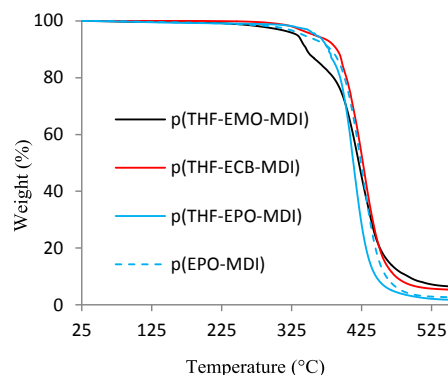
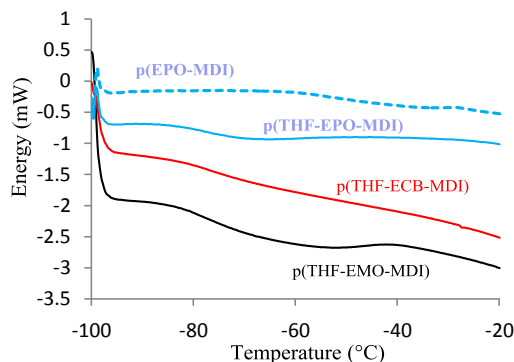


Fig.10. DSC of p(THF-EVO-MDI) polymers.<sup>‡</sup>



## Experimental

### General Procedure for Preparing p(THF-EVO).

Epoxidized cocoa butter<sup>45</sup> (50 g, 57 mmol) was added to dry tetrahydrofuran (250 mL) and the mixture stirred at 20 °C under  $\text{N}_2$  atmosphere for 30 minutes.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.81 g, 5.7 mmol) was added drop-wise and the mixture stirred for a further 24 hours at 20 °C. To the crude reaction was added saturated NaCl solution (200 mL) and chloroform (300 mL). The organic layer was washed with saturated  $\text{NaHCO}_3$  solution (100 mL), saturated NaCl solution (200 mL) and dried over anhydrous  $\text{MgSO}_4$ . Removal of solvent *in vacuo* yielded a clear viscous liquid (120 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3360 (O-H) 2921, 2850 (C-H) 1742 (C=O) 1105 (C-O) 754 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.24-5.28 (1H, m,  $\text{CH}_2\text{O}$ ) 4.25 (2H, dd,  $J$  = 11.9 Hz, 4.4 Hz,  $\text{CH}_2\text{O}$ ), 4.10 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.43 – 3.30 (64H, m,  $\text{HCO}$ ), 2.26 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.62-1.50 (72H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.30-1.18 (72H, m,  $\text{CH}_2\text{CH}_2$ ), 0.83 (9H, t,  $J$  = 6.8 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.2, 172.8 (C=O) 70.4 ( $\text{HC}-\text{O}$ ) 68.9 ( $\text{HC}-\text{O}$ ), 62.0, 61.8 ( $\text{H}_2\text{C}-\text{O}$ ), 33.9 ( $\text{O}=\text{CCH}_2$ ), 26.3 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.5, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ ).

## General Procedure for Polyurethane made from p(THF-EVO) and MDI.

P(THF-EPO), (10 g, hydroxyl value = 30.5 mg KOH/g sample) was dissolved in dry chloroform (150 mL) under N<sub>2</sub>. 4,4'-Methylene diphenyldiisocyanate (MDI) (1.7 g) was added. (The NCO/OH ratio index was 1.02). The reaction mixture was heated to 60 °C and the crude polyurethane was poured into a pre-heated mold at 60 °C. The polyurethane was cured at 60 °C for 24 hours.  $v_{\max}/\text{cm}^{-1}$  3308 (O=CNH) 2915, 2849 (C-H) 1729 (C=O) 1595 (aromatic =CH) 1098 (C-O) 721 (CH<sub>2</sub>).

## Conclusions

In conclusion, we have shown that it is possible to incorporate the renewable solvent THF into novel macromonomer polyols derived from renewable epoxidised oils by Lewis acid ring-opening reactions in THF as solvent. The degree of polymerisation, hydroxyl value and molecular weight can be controlled by varying the concentration, temperature, and amounts of Lewis acid catalyst and THF. These monomers contain primary hydroxyl groups (derived from ring-opening of THF) which are suited to react with MDI to furnish elastomeric polyurethanes. Comparison of the polyurethane derived from the monomer p(THF-EPO-MDI) with that derived from conventional ring-opening of epoxidised palm oil, p(EPO-MDI) indicated superior tensile strength [p(THF-EPO-MDI) = 9.1 MPa vs p(EPO-MDI) = 1.5 MPa] and elongation at break [p(THF-EPO-MDI) = 425% vs p(EPO-MDI) = 70%] with little compromise on thermal stability [p(THF-EPO-MDI) T<sub>10%</sub> = 378 °C, T<sub>50%</sub> = 414 °C, p(EPO-MDI) T<sub>10%</sub> = 379 °C T<sub>50%</sub> = 424 °C]. In other words, undertaking ring-opening polymerisation of two renewable components, (epoxidized vegetable oils and THF), gives rise to polyols which can be used to make PU's with significantly improved elastic properties than those made from ring-opening of vegetable oils alone.

## Acknowledgements

We acknowledge the Malaysian Palm Oil Board for a scholarship for SSH.

## Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures and characterisation data, 400 MHz <sup>1</sup>H NMR, infra red spectra and MALDI-TOF-MS data for p(THF-EMO), p(THF-ECB), p(THF-EPO), p(EPO) and p(THF) polyols are described. Properties of polymers from screening experiments of Lewis acids, and effect of temperature and concentration are described, and representative GPC's provided. Details of instrumentation used and methods for acid and alcohol value measurements are described. Experimental procedures for the formation of polyurethanes are described as well as their infrared spectra]. See DOI: 10.1039/b000000x/

‡ DSC and TGA of samples were conducted in a Mettler Toledo TGA/DSC 1 system. For DSC analysis, the samples were scanned from -100 °C to 600 °C at a heating rate of 10 K per minute in the presence of nitrogen. For TGA analysis, the samples were scanned from 25 °C to 600 °C at a heating rate of 10 K per minute in the presence of nitrogen. Tensile strength and elongation at break of polyurethane samples were

determined according to EN ISO 529-4: 1997 (CEN1997a). European standard. Testing was conducted with an Instron 5800 universal testing machine with an initial cross-head speed of 1 mm/minute for 2 minutes and then 50 mm/minute.

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