PAPER

Copolymers of tetrahydrofuran and epoxidized vegetable oils: application to elastomeric polyurethanes†

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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 methyloleate 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) $T_{decomp10\%}$ = 378 °C, $T_{decomp50\%}$ = 414 °C, p(EPO-MDI) $T_{decomp10\%}$ = 379 °C $T_{decomp50\%}$ = 424 °C].

Introduction

Vegetable oils are important renewable platform chemicals.[1,2] In particular, the ability to easily chemically modify vegetable oils has made them attractive feedstocks for the polymer industry.[3–5] 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
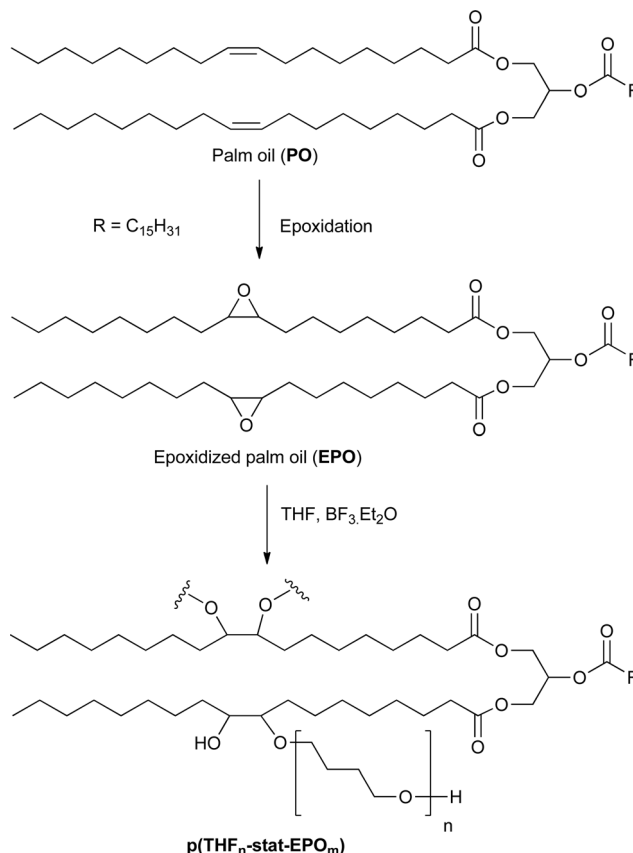
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‡ DSC and TGA of samples were conducted in a Mettler Toledo TGA/DSC 1 system. For DSC analysis, the samples were scanned from −100 °C to 600 °C at a heating rate of 10 K per minute in the presence of nitrogen. For TGA analysis, the samples were scanned 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.

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

Table 1 Screening of Lewis acids as potential catalysts in the reaction of EPO with THF to give p(THF-*stat*-EPO)†

Entry[a]	Lewis acid	Catalyst (mol%)	Conversion[b,c] (%)	M_n (kDa)	PDI
1	FeCl$_3$	10.0	90 (60)	17	2.6
2	SnCl$_4$	10.0	93 (77)	25	4.4
3	CF$_3$SO$_3$H	10.0	92 (79)	36	4.6
4	HBF$_4$	2.0[d]	95 (74)	22	3.8
5	BF$_3$·Et$_2$O	2.0[d]	97 (88)	56	6.5
6	BF$_3$·Et$_2$O	1.0	80[e]	45	3.2
7	BF$_3$·Et$_2$O	0.5	0	—	—
8	BF$_3$·Et$_2$O	2.5	Gelled	—	—

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

(20 : 0) unsaturated: 43.4% oleic (18 : 1), 10.0% linoleic (18 : 1) and 0.4% linolenic (18 : 3)][6] with 1.9 alkene groups per molecule on average, (Fig. 1).

Vegetable oils can be functionalized by reactions at the ester group (transesterification[7,8] or transamidation[9,10]) or the alkene functionality.[2] The most common approach to functionalization is at the alkene group (normally *via* epoxidation[11,12] and ring opening reactions[2]) but hydroformylation,[13,14] ozonolysis,[15,16] metathesis[17–22] and thiol–ene[23,24] 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.[5,25–29] 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.[30] An alternative approach to furnish primary polyols from vegetable oils utilizes ring-opening of epoxides with 1,3-propanediol.[31] Ionic-coordinative ring-opening polymerization[32] of epoxidized methyloleate (EMO) followed by LiAlH$_4$ reduction to give poly-ether polyols with molecular weights ranging between 0.9 and 7 kDa can also be used to make polyurethanes.[33] Polyol formation by ring-opening polymerization of epoxidised methyloleate (EMO) and epoxidized soybean oil (ESO) have been studied using HSbF$_6$ and BF$_3$·OEt$_2$ in dichloromethane respectively.[34,35] Polyether polyols derived from ESO exhibited thermally stable (>340 °C) highly cross-linked structures with glass transition temperatures between −16 and −48 °C.[35] After hydrolysis these cross-linked structures could be converted into hydrogels. Polyols (900–1200 g mol^{-1}) derived from HSbF$_6$ mediated ring-opening of EMO were reacted with 4,4′-methylene diphenyldiisocyanate (MDI) to make hard polyurethane rubbers,[34] while reaction with larger polyols (~7000 g mol^{-1}) furnished more flexible materials.[32]

Tetrahydrofuran (THF) is a relatively cheap industrial solvent that can be prepared from agricultural waste *via* succinic acid and is therefore potentially renewable.[36] Polytetrahydrofuran, p(THF), is obtained from homopolymerization of THF through cationic polymerization catalyzed by strong Lewis acids (BF$_3$, SbF$_5$) or strong Brønsted acids (FSO$_3$H, CF$_3$SO$_2$OSO$_2$CF$_3$).[37] One use of the p(THF) is to make elastomeric polyurethanes. The ring strain of THF (5.63 kcal mol^{-1}) is smaller than the ring strain of alkylene oxides (27.28 kcal mol^{-1})[38] 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.[39–41] One advantage of copolymerizing THF with EO or PO is the higher yield of polymers achievable (85–90%) compared to homopolymerization alone.[42] 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.[43]

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, Fig. 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$_3$·OEt$_2$, AlCl$_3$, SnCl$_4$)[37] or superacids (HBF$_4$, ClSO$_3$H, CF$_3$SO$_3$H).[44] In addition to these catalysts we screened FeCl$_3$, AlCl$_3$, TiCl$_4$, CF$_3$CO$_2$H and H$_2$SO$_4$ in the copolymerisation of
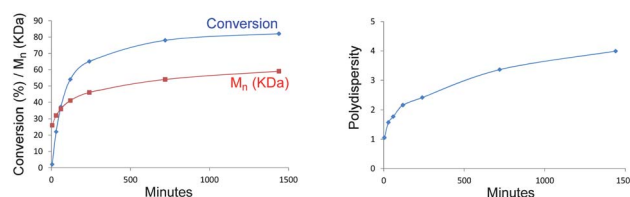

Fig. 2 M_n, conversion and PDI verses time for copolymerization of THF and EPO (20 : 1 w/w) with 1 mol% BF$_3$·Et$_2$O over 24 h.
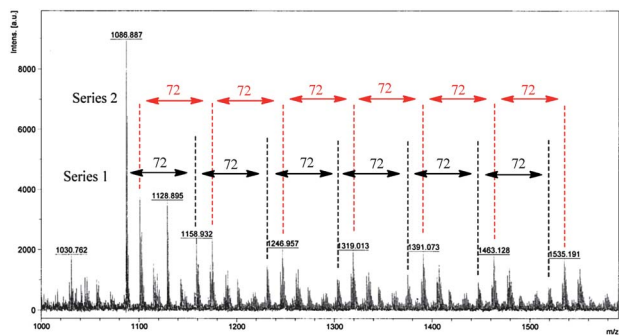
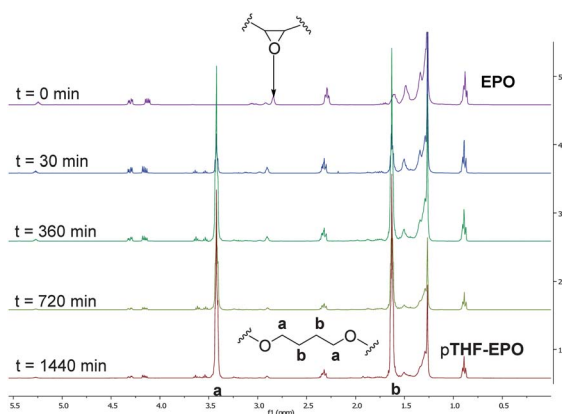Fig. 3 MALDI-TOF of p(THF-EPO) showing repeating unit of 72 Da.†

Fig. 4 400 MHz ^{1}H NMR of p(THF-EPO) verses time.†

epoxidized palm oil (EPO)[45] with THF at 20 °C with a 20 : 1 ratio of THF–EPO (w/w) over 24 h.†

Mixtures were analysed by GPC. Only 5 catalysts showed activity in the ring-opening process, (entries 1–5), Table 1. Both HBF$_4$ (entry 4) and BF$_3$·OEt$_2$ (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$_4$ we chose BF$_3$·OEt$_2$ 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,† (Fig. 3) and 400 MHz ^{1}H NMR† (Fig. 4) to

confirm incorporation of THF into the products. The change in % conversion, M_n and PDI were determined over time under the conditions shown for entry 6, Table 1 (Fig. 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$_2$O). 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, Fig. 3. For example series 1 shows a major peak at 1086.8 Da, which corresponds to the sodium adduct of p(THF$_2$-*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$_4$-*stat*-EPO) where the EPO had three C18 derived fatty acids but 2 initial epoxide groups. Analysis of the ^{1}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.

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 (0.38 M 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 (Fig. 5). Decreasing the concentration of EPO in
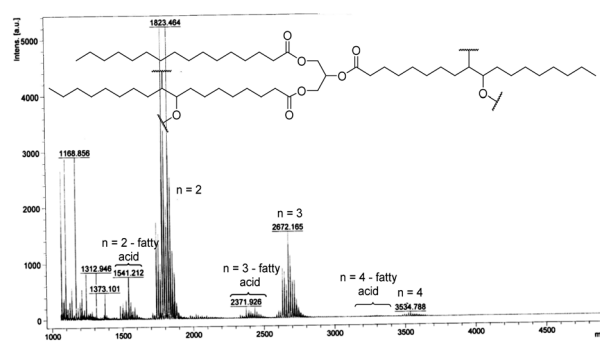

Fig. 5 MALDI-TOF-MS for the homopolymerisation of EPO.[48]

Table 2 Effect of concentration and temperature on homo- and co-polymerization of EPO with and without THF

Entry	Conc. (M)	Temp. (°C)	Solvent	BF$_3$·Et$_2$O (mol %)	Conver.^{a} (%)	M_n (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

^{a} Percentage determined from GPC.

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

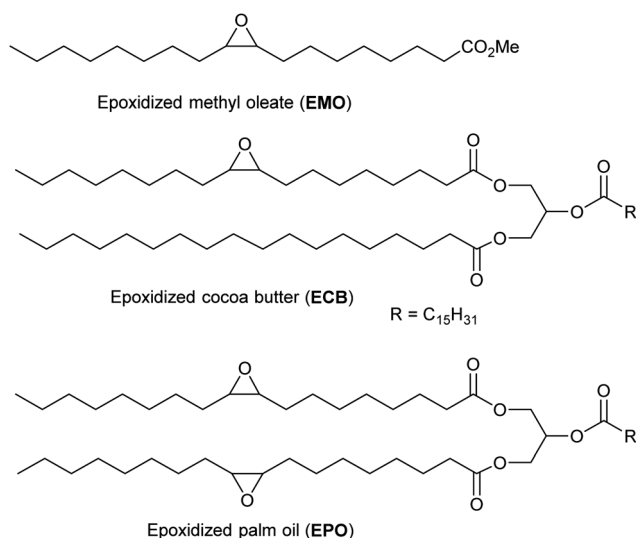| Entry	EVO	BF$_3$·Et$_2$O (mol%)	THF–EVO	Conver. (%)	M_n (kDa)	PDI
1	EMO	2.5	20 : 1	75	8k	2.2
2	EMO	5.0	20 : 1	97	26k	2.1
3	ECB	5.0	20 : 1	82	16k	2.3
4	ECB	10.0	20 : 1	93	30k	2.8
5	EPO	2.0	12 : 1	Gelled	—	—
6	EPO	2.0	16 : 1	79	45k	3.2
7	EPO	2.0	24 : 1	83	56k	3.0

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

hexane (0.19 M, 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 8 with Table 2, entry 5). This is likely due to the higher activation energy for THF ring-opening (51.3 kcal mol^{-1}) compared to epoxide ring-opening (20 kcal mol^{-1}).[46] We also prepared p(THF) by the method of Dorai[47] as a benchmark for our study on PU's.

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$_2$Cl$_2$.[32–34] 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. 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 (Fig. 6).

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.

The thermal properties for the co-polymers were also obtained (Fig. 7). The thermal stability of all three p(THF-EVO) polyols is greater than for conventional p(THF), or p(THF-PO) alone.[41] The $T_{50\%}$ 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.[41] The major decomposition mode for the p(THF-EVO)'s is likely to be due to THF depolymerisation.[41] As expected the thermal stability significantly increases for the triglyceride derivatives compared to p(THF-EMO), Table 4. A slight increase in $T_{10\%}$ also occurs in the p(THF-EVO) series with increasing M_n and PDI's [$T_{10\%}$ 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 $T_{10\%}$ p(THF-EPO) = 386 °C with p(EPO) = 371 °C).

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 and 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. Fig. 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.[50]

Thermal analysis was carried out on the three novel p(THF-EVO-MDI) polymers and comparison made between p(EPO-MDI), Fig. 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.[25,29,52] Vegetable oil derived polyurethanes normally show two-step degradation.[52] The first small step is degradation of the urethane bond to give primary amines and alkenes, isocyanates or alcohols or secondary amines[33,53] followed by the main loss of weight above 350 °C due to

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

Entry	Polymer	OH value[a] (mg KOH per g)	Acid value[a] (mg KOH per g)	M_n (kDa)	PDI	$T_{10\%}$[b] (°C)
1	P(THF-EMO)	25	7	26k	2.1	345
2	P(THF-ECB)	27	1	30k	2.8	374
3	P(THF-EPO)	40	1	56k	3.0	386
4	P(EPO)	38	1	16k	3.1	371

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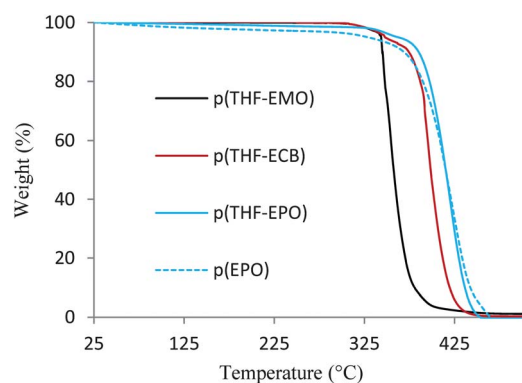

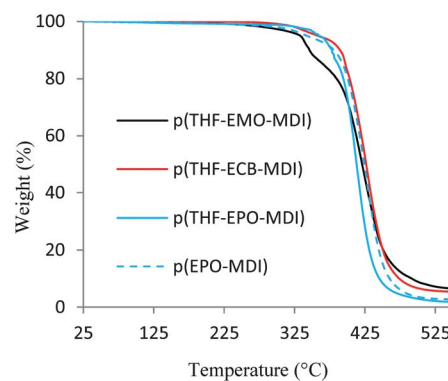Fig. 7 TGA of p(THF-EVO) polymers.‡
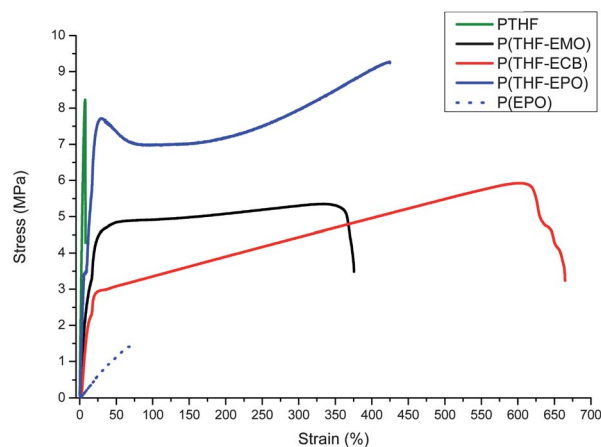

Fig. 9 TGA of p(THF-EVO-MDI) polymers.‡

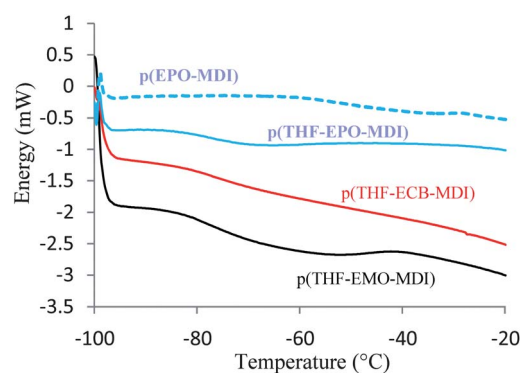Fig. 8 Stress–strain curves of p(THF-EVO-MDI) polymers.‡

Fig. 10 DSC of p(THF-EVO-MDI) polymers.‡

polyether chain scission.[52] 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.[52] 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 are 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%).[51] Both the polymers derived from methyloleate 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 per g) than for that derived from palm oil p(THF-EPO). Therefore, the cross-link densities exhibited by the methyloleate and cocoa butter derived polymers, p(THF-EMO-MDI), entry 2, and p(THF-ECB-MDI), were relatively low (3.2–3.4 × 10^{-4} mol cm^{-3}) compared to that derived from palm oil, p(THF-EPO-MDI), 5.3 × 10^{-4} mol cm^3. 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

Table 5 Properties of PU samples made from p(THF), p(THF–EVO) and p(EVO)‡

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

from methyloleate and cocoa butter with p(THF-ECB-MDI), entry 3, significantly higher than for methyloleate 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. BF$_3$·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.

Experimental

General procedure for preparing p(THF–EVO)

Epoxidized cocoa butter[45] (50 g, 57 mmol) was added to dry tetrahydrofuran (250 mL) and the mixture stirred at 20 °C under N$_2$ atmosphere for 30 minutes. BF$_3$·Et$_2$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 NaHCO$_3$ solution (100 mL), saturated NaCl solution (200 mL) and dried over anhydrous MgSO$_4$. Removal of solvent *in vacuo* yielded a clear viscous liquid (120 g). ν_{max}/cm^{-1} 3360 (O–H) 2921, 2850 (C–H) 1742 (C=O) 1105 (C–O) 754 (CH$_2$); ^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 5.24–5.28 (1H, m, C*H*O) 4.25 (2H, dd, J = 11.9 Hz, 4.4 Hz, C*H*$_2$O), 4.10 (2H, dd, J = 11.9 Hz, 5.9 Hz, C*H*$_2$O), 3.43–3.30 (64H, m, *H*CO), 2.26 (6H, t, J = 7.5 Hz, O=CC*H*$_2$CH$_2$), 1.62–1.50 (72H, m, O=CCH$_2$C*H*$_2$CH$_2$, C*H*$_2$CH$_2$O), 1.30–1.18 (72H, m, C*H*$_2$CH$_2$), 0.83 (9H, t, J = 6.8 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz CDCl$_3$): δ_C = 173.2, 172.8 (C=O) 70.4 (H*C*–O) 68.9 (H*C*–O), 62.0, 61.8 (H$_2$*C*–O), 33.9 (O=C*C*H$_2$), 26.3 (O=CCH$_2$*C*H$_2$CH$_2$, *C*H$_2$CH$_2$O), 29.5, 22.4 (CH$_2$*C*H$_2$CH$_2$), 13.9 (CH$_2$*C*H$_3$).

General procedure for polyurethane made from p(THF–EVO) and MDI

P(THF-EPO), (10 g, hydroxyl value = 30.5 mg KOH per g sample) was dissolved in dry chloroform (150 mL) under N$_2$. 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. ν_{max}/cm^{-1} 3308 (NH) 2915, 2849 (C–H) 1729 (C=O) 1595 (aromatic =CH) 1098 (C–O) 721 (CH$_2$).

Conclusions

In conclusion, we have shown that it 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) $T_{10\%}$ = 378 °C, $T_{50\%}$ = 414 °C, p(EPO-MDI) $T_{10\%}$ = 379 °C $T_{50\%}$ = 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.

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