

Strategies for synthesis of epoxy resins from oleic acid derived from food wastes.

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Abstract

The use of biomass-sourced chemical feedstocks creates a conflict over land use between food and fuel/chemical production. Such conflict could be reduced by making use of the annual 1.3 Pg food waste resource. Oleic acid is available from seed oils such as pumpkin, grape, avocado and mango. Its esterification with diols 1,3-propanediol, resorcinol and orcinol was used to form diesters and the naturally occurring norspermidine was used to prepare a diamide, all under ambient conditions. These compounds were then epoxidised and polymerised. When esterification was followed by epoxidation and subsequent curing at elevated temperature with *p*-phenylenediamine or diethylenetriamine, hard insoluble resins were formed. When the sequence was changed such that the epoxidized oleic acid was first reacted with cis-1,2-cyclohexanedicarboxylic anhydride and then esterified with orcinol and resorcinol, insoluble crosslinked polymers were also obtained.

A study of the interaction between the precursors and their respective epoxides with untreated montmorillonite and five organically modified clays was made with the purpose of exploring the scope for nano-composite polymer production. Neither oleic acid nor epoxystearic acid demonstrated significant intercalation in unmodified montmorillonite clay even after 7.8 Ms. However, a quaternary ammonium pretreated clay, Cloisite 10A was swollen by oleic acid. This provides a potential route to generate *in-situ* polymerized nanocomposites in which both matrix and reinforcement have low embodied fossil carbon.

Keywords: oleic acid, biomass, epoxy resins, esterification, nanocomposites

Introduction Petroleum is the main feedstock for monomer and polymer production and nearly 7% of world oil and gas is used for their manufacture¹. More challenging extraction methods are likely to increase the background petroleum price in the long term so that biomass becomes increasingly viable as a chemical feedstock²⁻⁴. The literature on biomass-derived polymers has been dormant while petrochemicals dominated the market but is now expanding to reflect interest in ‘sustainable’ technologies⁵⁻⁷ and plant oils are a focus for this attention^{8,9}. The conversion of land-use in poorer communities from food to biofuel production has caused conflict which would recur, *mutatis mutandi*, for chemical feedstock production^{10,11}. It has thus been argued¹² that the industrial fraction of the 1.3 Pg per annum food waste resource can be exploited for materials production thus lessening land-use conflict. Food waste scales with population as does the demand for materials. Vegetable oils are triglyceride-based, generally liquids at room temperature with 94~96 wt.% fatty acids¹³ which can be differentiated by carbon chain length and the positions of double bonds, typically 14~22 carbon atoms and 0 to 3 alkenyl degrees of unsaturation¹⁴. The configuration and distribution of fatty acids influences the physical and chemical properties of materials produced from them¹⁵.

The objective here was to explore the synthesis of novel epoxy resins using a food waste, oleic acid, as the feedstock. World annual production of mango is 36 Tg and mango seed oil contains 40% oleic acid, grape seed oil 15-20%, pumpkin seed oil 32% and avocado seed oil 17%, so industrial and agricultural food waste can be a significant source of oleic acid: consumer food waste is generally too contaminated to be a suitable resource.

Unsaturated fatty acids are obtained by treating triglycerides with sodium hydroxide followed by separation. They have at least one alkene functional group which may be epoxidized. These can undergo polymerisation reactions based on a succession of intermolecular cross-linkages via epoxide ring openings. As the extent of cross-linking increases, the resin becomes progressively more solid and less soluble¹⁶.

Epoxy resins can be cured by nucleophile initiated direct reaction between two resin molecules (homopolymerisation)¹⁷ and ring opening by photoinitiators (cationic photopolymerisation)¹⁸ but the most common and important methods are those which use a curing agent or hardener (copolymerisation). These can be polyfunctional amines, cyclic anhydrides or polyphenols¹⁹. The many types of epoxy resins, curing processes and additives (such as plasticizers and reactive diluents) give rise to materials with a wide range of properties in applications such as paints, adhesives and composites^{16,20}.

Natural unsaturated fatty acids tend to occur as *cis*-isomers. Oil is extracted from seed waste by pressing and oleic acid can be isolated by low temperature crystallisation. Epoxidation of oleoyl unsaturations can be achieved by the action of peroxides or peracids. Two common reagents used

for this purpose are *meta*-chloroperbenzoic acid (*m*CPBA)²¹ and hydrogen peroxide (H₂O₂)¹⁵. Previous investigations have found that epoxidation using H₂O₂ works best in the presence of an organic acid such as acetic or formic acid, which forms a peracid with the peroxide^{15,22}. The carboxylic group in oleic acid could potentially be used to replace added carboxylic acids for *in-situ* peracid generation as, according to Fong, et al.²³, peracid could be generated when the ester group and hydrogen peroxide are combined. However, this reaction can only happen either at pH around 10 or in the presence of catalyst^{23,24}.

Epoxy resins with two epoxide groups per molecule can be cured using polyamines without needing a catalyst or solvent^{19,22}. Possible polyamine hardeners include triethylenetetramine (TETA) and *p*-phenylenediamine (PPD). Diepoxides that may be appropriate for this procedure are epoxidized dioleates (diesters of oleic acid) or dioleamides (diamides of oleic acid). Dioleates may be prepared at room temperature via a Steglich esterification between oleic acid and a diol such as orcinol or resorcinol, by using 4-(dimethylamino)pyridine (DMAP) and *N,N'*-dicyclohexylcarbodiimide (DCC)²⁵. Reaction of the extract from aloes²⁶ or the plant resin asafoetida²⁷ with potassium hydroxide can be used to produce orcinol or resorcinol respectively. Dioleamides may be prepared at room temperature by reaction of oleoyl chloride with a polyamine²⁸⁻³⁰.

Norspermidine possesses two primary amines and one sterically hindered secondary amine group. It can therefore be used to prepare a dioleamide. Although toxic, norspermidine occurs naturally in a number of plants, algae and bacteria such as Lucerne³¹, red algae³² and *V. parahaemolyticus*³³.

One of the most straightforward methods to produce oleic acid-based polymers is via homopolymerisation: epoxidation of the acid followed by cross-linking directly between the epoxide groups. Previous investigations have shown that these processes often demand high curing temperatures of 100-200 °C applied for periods of 1-4 hours for effective cross-linking to be achieved, but that a solvent is not usually needed³⁴. Homopolymerisation also requires a Lewis base initiator to proceed such as piperidine, *p*-phenylenediamine (PPD) or triethylamine (NEt₃)^{17,34}. One promising route to thermosetting materials from biomass is the crosslinking of epoxidized sucrose esters of fatty acids³⁵ for uses in coatings, adhesive and composites and tensile strengths of 18 MPa have been obtained³⁶.

The two main classes of crosslinking agents applied to epoxides for polymerization are amines and anhydrides. Such reactions have been widely studied^{37,38}. The amine curing process takes place at the stoichiometric ratio³⁷ and room temperature as amines exhibit high nucleophilicity. Anhydride curing has been studied for the last 50 years³⁹. Usually an initiator is used as the epoxy/anhydride does not react directly and therefore an active hydrogen must open the

ring of the anhydride curing agent first^{40,41}. In this case, a tertiary amine was used as initiator (triethylamine).

The use of biomass for preparing structural resins is not new. In the interwar years, Henry Ford invested heavily in the use of soybean oil in vehicle manufacture⁴². The use of smectite clays for reinforcing polyamides also originated in the motor industry in 1985⁴³ and such polymer-clay nanocomposites have expanded⁴⁴ to provide materials with superior elastic modulus, strength, heat distortion and barrier properties. Three types of composite are seen: (a) a conventional composite in which the polymer does not enter the galleries, (b) an intercalated nanocomposite in which the polymer distributes itself throughout the galleries but the clay layers remain stacked and (c) an exfoliated nanocomposite in which clay layers are dispersed and separated. The last is preferred as it provides superior properties but actually most nanocomposites contain both exfoliated and intercalated fractions. Such nanocomposites can be made by melt intercalation, solution intercalation and in-situ intercalative polymerization in which the unreacted polymer precursors are hosted by the galleries before reacting. Such composites, prepared from food waste derived polymers offer the prospect of a composite material with extremely low embodied fossil carbon.

In this work, two approaches to form oleic acid-based polymers have been used. First, oleic acid was coupled to diols and a diamine to give two alkenyl groups per molecule then epoxidized and polymerized. In an alternative approach oleic acid was first epoxidized then reacted with anhydride to crosslink and then esterified.

EXPERIMENTAL

Materials and Measurements

The major component of mango butter is oleic acid (40-46%) which can be separated from other components (mainly stearic at 40-45% with palmitic, linoleic and arachidic together ~10%) by crystallization of saturated acids from aqueous acetone solution at -25 °C^{45,46} to give the oleic acid at >90% purity. In this work, commercially available oleic acid at 90% (Sigma Aldrich Chemical Co, Gillingham, UK) was used in the synthesis of monomers. It is envisaged that impurities will be comparable to those in technical grade oleic acid and will not influence the epoxidation reaction.

Orcinol, resorcinol, oleic acid (90%), 4-(dimethylamino) pyridine, *N,N'*-dicyclohexylcarbodiimide, hexane, ethyl acetate, norspermidine, pyridine, benzene, oleoyl chloride, acetone, *meta*-chloroperbenzoic acid, diethylenetriamine, titanium (IV) *n*-butoxide (99%) and *p*-phenylenediamine were purchased from Sigma Aldrich Chemical Co, Gillingham, UK. Triethylamine, Geduran® silica gel 60 and 30% hydrogen peroxide were from Merck KGaA, Darmstadt Germany. Formic acid (98%) was from VWR Lutterworth UK. Toluene and dichloromethane were purchased from Fisher Scientific, Loughborough UK. 1,3-Propanediol and

cis-1,2-cyclohexanedicarboxylic anhydride were purchased from Alfa Aesar. Deuterated chloroform CDCl₃ (99.8%) was purchased from Apollo scientific, Heysham UK. The montmorillonites used were Nanofil 116® and Cloisite® 10A (Rockwood Company, Southern Clay Products Inc. Texas USA) and in some cases were modified as described below. Other reagents were used as supplied without modification or purification.

IR spectra were taken on a Bruker-FTIR-ALPHA Platinum ATR with a single reflection diamond ATR module with a scan rate of 16 and a wavelength range from 4000 to 600 cm⁻¹. A Siemens D500 diffractometer with Cu Kα₁ radiation (λ = 1.54056 Å) was used for X-ray diffraction measurements with a scanning step of 0.05° and a scan time of 4 seconds per step. Mass spectra were recorded on a Waters Acquity uPLC SQD using HPLC grade water and acetonitrile (both with 0.1% formic acid) as the solvents. Solution NMR spectra were recorded on Bruker spectrometers AMX300, Avance 500 and Avance III 600, with ¹H NMR Larmor frequencies of 300, 500 and 600 MHz, respectively. Chemical shifts (in ppm) relative to tetramethylsilane (TMS) were calibrated using the residual solvent peak (¹H 7.26 ppm in CDCl₃). Coupling constants (*J*) were measured in Hertz (Hz) and multiplicities for ¹H NMR coupling are expressed as s (singlet), d (doublet), t (triplet), quint (quintet), and m (multiplet). A Bruker Avance 300 NMR spectrometer with a 7.05 T wide-bore magnet and a 4 mm magic-angle spinning (MAS) probe was used to record solid-state NMR spectra. High-resolution solid-state ¹³C NMR spectra at 75.5 MHz were recorded at ambient probe temperature using cross-polarization (CP), MAS (8 kHz), high-power proton decoupling (HPPD) and total suppression of spinning sidebands (TOSS). Typical acquisition conditions were: ¹H 90° pulse duration 2.45 μs; contact time 2 ms; recycle delay 5 s. ¹³C CPMAS TOSS spectra with non-quaternary suppression (NQS) were also acquired with a 50 μs dephasing delay to suppress signals from motionally rigid CH and CH₂ carbons. For direct detection of ¹³C nuclei with HPPD, the ARINGDEC pulse sequence was used with suppression of probe ringdown effects, which also suppresses the background signal. Typical acquisition conditions were: ¹³C 90° pulse duration = 3.0 μs; recycle delay = 15 s. The solid-state ¹³C NMR chemical shifts are expressed relative to TMS by using the resonance line at 176.46 ppm for the α polymorph of glycine as an external standard.

Monomer synthesis and purification.

Diesters To oleic acid (2.2 equiv.), diols 1,3-propanediol (1.0 equiv.), orcinol (1.0 equiv.) or resorcinol (1.0 equiv.) in dichloromethane (CH₂Cl₂) at 0 °C was added 4-(dimethylamino)pyridine (DMAP) (0.03 equiv.) and then *N,N'*-dicyclohexylcarbodiimide (DCC) (2.4 equiv.). The reaction was stirred for 24 h at room temperature, the solid formed was removed by filtration and the solvent

removed *in vacuo*. Either crude material was directly carried through to the next epoxidation step or was purified by column chromatography as detailed below.

Oleate propyl diester diol⁴⁷ The reaction was carried out using oleic acid (69 g, 0.22 mol; 90% purity), 1,3-propanediol (7.6 g, 0.10 mol), DMAP (3.6 g, 0.03 mol) and DCC (49.4 g, 0.24 mmol) in CH₂Cl₂ (200 mL). The urea precipitate formed was removed by filtration and product isolated from the filtrate (32 g, 53%). NMR spectroscopic analysis indicated that the product was isolated in > 90% purity so it was taken directly through to the next epoxidation step. ¹H NMR (300 MHz; CDCl₃) δ 5.29-5.35 (4H, m, 2 × CH=CH), 4.14 (4H, t, *J* 6.0 Hz, 2 × CH₂OCO), 2.29 (4H, t, *J* 7.5 Hz, 2 × CH₂CO), 1.93-2.03 (10H, m, 4 × =CHCH₂, CH₂CH₂O), 1.58-1.63 (4H, m, 2 × CH₂), 1.19-1.34 (40H, m, 20 × CH₂), 0.87 (6H, t, *J* 6.0 Hz, 2 × CH₂CH₃).

Orcyl dioleate The reaction was carried out using oleic acid (17.28 g, 55.1 mmol; 90% purity), orcinol (3.10 g, 25.0 mmol), DMAP (0.092 g, 0.75 mmol) and DCC (12.4 g, 60.0 mmol) in CH₂Cl₂ (100 mL). The product was purified by column chromatography (hexane/ethyl acetate 30:1) to give orcyl dioleate as a pale yellow oil (7.59 g, 47%). ¹H NMR (500 MHz; CDCl₃) δ 6.77 (2H, s, ArH), 6.68 (1H, s, ArH), 5.30-5.41 (4H, m, 2 × CH=CH), 2.52 (4H, t, *J* 7.5 Hz, 2 × CH₂CO), 2.35 (3H, s, ArCH₃), 1.91-2.09 (8H, m, 4 × =CHCH₂), 1.68-1.78 (4H, quint, *J* 7.5 Hz, 2 × CH₂CH₂CO), 1.19-1.44 (40H, m, 20 × CH₂), 0.84-0.93 (6H, t, *J* 7.0 Hz, 2 × CH₂CH₃); *m/z* (CI⁺) 653 (M⁺, 67%), 265 (CH₃(CH₂)₇HC=CH(CH₂)₇CO⁺, 100%).

Resorcyl dioleate The reaction was carried out using oleic acid (17.3 g, 55.1 mmol; 90% purity), resorcinol (2.77 g, 25.2 mmol), DMAP (0.092 g, 0.75 mmol) and DCC (12.4 g, 60.0 mmol) in CH₂Cl₂ (100 mL). The product was purified by column chromatography (hexane/ethyl acetate 30:1) to give resorcyl dioleate as a pale yellow oil (13.2 g, 82%). ¹H NMR (500 MHz; CDCl₃) δ 7.34 (1H, t, *J* 8.0 Hz, ArH), 6.95 (2H, d, *J* 8.0 Hz, ArH), 6.89 (1H, s, ArH), 5.30-5.41 (4H, m, 2 × CH=CH), 2.53 (4H, t, *J* 6.8 Hz, CH₂CO), 1.93-2.10 (8H, m, 4 × =CHCH₂), 1.73 (4H, quint, *J* 6.8 Hz, 2 × CH₂CH₂CO), 1.19-1.46 (40H, m, 20 × CH₂), 0.87 (6H, t, *J* 7.0 Hz, 2 × CH₂CH₃); *m/z* (CI⁺) 639 (M⁺, 71%), 265 (CH₃(CH₂)₇(CH)₂(CH₂)₇CO⁺, 100%).

Norspermidine dioleamide⁴⁸ To norspermidine (1.28 g, 9.75 mmol) and pyridine (1.65 g, 20.9 mmol) in benzene (50 mL), oleoyl chloride (6.03 g, 20.0 mmol) was added dropwise at ambient temperature. The solution was stirred for 15 min and the resulting solid separated by filtration under reduced pressure and then recrystallised from acetone (twice) to give norspermidine dioleamide as a yellow solid (2.63 g, 41%). Mp 248-256 °C (acetone); ¹H NMR (500 MHz; CDCl₃) δ 6.78-6.90 (2H, br s, RCONH), 5.30-5.40 (4H, m, 2 × CH=CH), 3.40 (4H, t, *J* 7.0 Hz, 2 × CONHCH₂), 2.96 (4H, t, *J* 7.0 Hz, 2 × CH₂NH), 2.25 (4H, t, *J* 6.5 Hz, 2 × CH₂CO), 2.13 (4H, quint, *J* 7.0 Hz, 2 ×

NHCH₂CH₂), 1.92-2.09 (8H, m, 4 × =CHCH₂), 1.71-1.80 (1H, br s, CH₂NHCH₂), 1.66 (4H, quint, *J* 6.5 Hz, 2 × CH₂CH₂CO), 1.18-1.40 (40H, m, 20 × CH₂), 0.86 (6H, t, *J* 7.0 Hz, 2 × CH₂CH₃); *m/z* (ES⁺) 660 (M⁺, 100%), 396 (RCONH(CH₂)₃NH(CH₂)₃NH⁺, 44%).

Epoxidation reactions

Two epoxidation methods were used, with either hydrogen peroxide^{15,49} or *meta*-chloroperbenzoic acid: the highest yielding preparations are described below:

9,10-Epoxystearic acid: To a stirred solution of oleic acid (90%; 3.57 g, 11.3 mmol) in toluene (30 mL) was added formic acid (95%; 1.9 mL, 47.8 mmol) and the reaction was heated to 80 °C. Hydrogen peroxide solution was then added dropwise (54.8 mL, 546 mmol; 30% solution). The reaction was then cooled to room temperature, separated and the organic phase washed with water (3 × 20 mL), dried (MgSO₄), and evaporated to give 9,10-epoxystearic acid (1.38 g, 41%) as a pale yellow waxy solid. Mp 56-59 °C (lit., Mp 59.5 °C⁵⁰); ¹H NMR (500 MHz; CDCl₃) δ 9.27-11.18 (1H, br s, COOH), 2.91 (2H, m, CHOCH), 2.35 (2H, t, *J* 6.5 Hz, CH₂CO₂H), 1.64 (2H, quint, *J* 6.5 Hz, CH₂CH₂CO₂H), 1.42-1.56 (4H, m, CH₂CHOCHCH₂), 1.16-1.45 (20H, m, 10 × CH₂), 0.87 (3H, t, *J* 7.0 Hz, CH₂CH₃); *m/z* (ES⁻) 297 ([M-H]⁻, 100%).

9,10-Epoxystearate propyl diester diol To a stirred solution of oleate propyl diester diol (6.08 g, 10.0 mmol) in toluene (5 mL) was added formic acid (0.74 mL, 20 mmol). Hydrogen peroxide solution was then added dropwise (2 mL, 20 mmol; 30% solution), followed by raising the temperature slowly to 80 °C. The reaction was cooled to room temperature, separated and the organic phase washed with water (2 × 50 mL), dried (MgSO₄), and evaporated to give 9,10-epoxystearate propyl diester diol (3.18 g, 50%; ~ 50% purity with oleate propyl diester diol remaining) as a pale yellow wax/syrup. ¹H NMR (500 MHz; CDCl₃) δ 4.14 (4H, t, *J* 6.5 Hz, 2 × CH₂OCO), 2.91 (4H, m, 2 × CHOCH), 2.33 (4H, m, 2 × CH₂CO₂), 1.96 (2H, m, CH₂CH₂OCO), 1.55-1.70 (8H, m, 4 × CH₂), 1.16-1.54 (40H, m, 20 × CH₂), 0.91 (6H, t, *J* 6.7 Hz, 2 × CH₂CH₃).

Orcyl-di-9,10-epoxystearate. To orcyl dioleate (1.26 g, 1.93 mmol) in chloroform (20 mL) *m*CPBA (2.21 g, 9.86 mmol; 77% purity) was added. The mixture was stirred at room temperature for 1.5 h. The resulting precipitate of *meta*-chlorobenzoic acid by-product was removed by filtration, and the filtrate was washed with 5% sodium hydrogen carbonate, dried (MgSO₄) and the solvent removed *in vacuo* to yield orcyl-di-9,10-epoxystearate (1.15 g, 87%) as a yellow oil. ¹H-NMR (500 MHz; CDCl₃) δ 6.79 (2H, s, ArH), 6.71 (1H, s, ArH), 2.92 (4H, m, 2 × CHOCH), 2.53 (4H, t, *J* 7.5 Hz, 2 × CH₂CO₂), 2.36 (3H, s, ArCH₃), 1.74 (4H, quint, *J* 7.5 Hz, 2 × CH₂CH₂CO₂), 1.51 (8H, m, 2 × CH₂CHOCHCH₂), 1.18-1.47 (40H, m, 20 × CH₂), 0.90 (6H, t, *J* 7.0 Hz, 2 × CH₂CH₃); *m/z* (ES⁺) 685 (M⁺, 100%).

Resorcyl-di-9,10-epoxystearate. To resorcyl dioleate (4.78 g, 7.48 mmol) in chloroform (40 mL) *m*CPBA (9.18 g, 41.0 mmol; 77% purity) was added. The mixture was stirred at room temperature for 1.5 h. The resulting precipitate of *meta*-chlorobenzoic acid by-product was removed by filtration, and the filtrate was washed with 5% sodium hydrogen carbonate, dried (MgSO₄) and the solvent removed *in vacuo* to yield resorcyl-di-9,10-epoxystearate (3.86 g, 77%) as a pale yellow wax. Mp 27-33 °C; ¹H-NMR (500 MHz; CDCl₃) δ 7.37 (1H, t, *J* 8.5 Hz, *ArH*), 6.97 (2H, d, *J* 8.5 Hz, *ArH*), 6.92 (1H, s, *ArH*), 2.88-2.96 (4H, m, *CHOCH*), 2.52 (4H, t, *J* 6.5 Hz, 2 × *CH*₂CO₂), 1.67-1.78 (4H, m, 2 × *CH*₂CH₂CO₂), 1.48-1.58 (8H, m, 2 × *CH*₂CHOCHCH₂) 1.18-1.48 (40H, m, 20 × CH₂), 0.84-0.95 (6H, m, 2 × CH₂CH₃); *m/z* (CI⁺) 671 (M⁺, 59%), 281 (CH₃(CH₂)₇CHOCH(CH₂)₇CO⁺, 100%).

Norspermidyl di-9,10-epoxystearamide. To a stirred solution of norspermidine dioleamide (0.970 g, 1.47 mmol) in toluene (20 mL) was added formic acid (95%; 3.3 mL, 83.1 mmol), and the reaction was heated to 80 °C. Hydrogen peroxide solution was added dropwise (5.95 g, 52.5 mmol; 30% solution). The reaction was then cooled to ambient temperature, separated and the organic phase washed with water (3 × 30 mL), dried (MgSO₄), and evaporated to give norspermidyl di-9,10-epoxystearamide (0.61 g, 60%) as a yellow paste. ¹H-NMR (500 MHz; CDCl₃) δ 6.58-7.08 (2H, br s, RCONH), 3.46 (4H, t, *J* 6.0 Hz, 2 × CONHCH₂), 2.94-3.00 (4H, m, CH₂NHCH₂), 2.87-2.97 (4H, m, *CHOCH*), 2.29 (4H, t, *J* 6.5 Hz, 2 × CH₂CONH), 2.11 (4H, quint, *J* 6.5 Hz, 2 × NHCH₂CH₂), 1.74-1.85 (1H, br s, CH₂NHCH₂), 1.60-1.69 (4H, quint, *J* 6.5 Hz, 2 × CH₂CH₂CONH), 1.32-1.44 (8H, m, CH₂CHOCHCH₂), 1.18-1.32 (40H, m, 20 × CH₂), 0.86 (6H, t, *J* 7.0 Hz, CH₂CH₃); *m/z* (ES⁺) 692 (M⁺, 25%).

Amine-epoxy Reactions

For the homopolymerization of 9,10-epoxystearic acid, 1 eq. and PPD/NEt₃ initiator (0.05 eq.) were mixed, placed in a glass sample tube and heated in an oven at 100 °C/150 °C/200 °C for 1 h or 5 h.

For the epoxy dioleates, two amine curing agents were used, (i) diethylenetriamine (DET) and (ii) *p*-phenylenediamine (PPD) using the following procedures. The diepoxy compounds and diamine curing agents were mixed in 1:1 equivalents at ambient temperature until a homogeneous mixture was obtained. In some cases it was left to react for up to seven days (0.6 Ms) and in others it was heated in an oven at 150 °C for 16 h.

Anhydride Curing Reactions

Initially, the anhydride curing step using cis-1,2-cyclohexanedicarboxylic anhydride (CH) with triethylamine (NEt₃) as initiator was applied after esterification and epoxidation. The epoxidized monomer, CH and NEt₃ were mixed in molar ratios of 0.5/0.5/0.0085, respectively. The curing time and temperature were prompted by the work of Nicolau *et al.*¹⁵ which used 165 °C for 3 hours and by Rosch *et al.*⁵¹, who used 200 °C for 1 hour. Products were stored in a vacuum desiccator at room temperature.

In subsequent experiments, the epoxidized but unesterified oleic acid (9,10-epoxystearic acid) was reacted with anhydride curing agent. The reaction product was subsequently mixed with one of the diols (1,3-propanediol, orcinol or resorcinol) in a round bottom flask in a molar ratio of 2:1. The mixture was raised to 160 °C by use of a silicone oil bath and 0.01 mL of titanium (IV) n-butoxide was added to the mixture⁵². Reaction took place for 1 hour after which the temperature was decreased to 120 °C for 30 minutes in order to remove all water produced from the esterification reaction. Solubility tests were performed on the polymers thus obtained.

Interaction with smectite clays

XRD was used to assess swelling in order to explore the viability of forming polymer-clay nanocomposites by *in-situ* polymerization. Samples of (i) clay, (ii) clay + methanol and (iii) clay + monomer + methanol were made using 1 g of monomer, 1 g of clay and 10 mL of methanol. All the samples were exposed for 10 min to the ultrasonicator at a duty cycle 0.5 with constant amplitude of 60% with the exception of organoclay which was hand mixed. A control with solvent and clay alone were used to establish the effect of solvent on the clay. All samples were dried at 60 °C overnight to remove solvent.

Five different clays were used: (i) Nanofil 116®, an unmodified montmorillonite (Rockwood Company, Southern Clay Products Inc. Texas USA) (ii) Cloisite® 10A which is modified with a benzyl (hydrogenated tallow alkyl)dimethyl, salt (Rockwood Company, Southern Clay Products Inc. Texas USA), (iii) Nanofil 116 treated with aminolauric acid (ALA modified), (iv) Nanofil 116 treated with diethylenetriamine (DET modified) and (v) Nanofil 116 treated with *p*-phenylenediamine (PPD modified). Clays (iii), (iv) and (v) were prepared in this laboratory by Mr Illya Litvinov following the procedure recommended by Akela *et al.*⁵³ A Siemens D500 diffractometer with Bragg-Brentano geometry and silicon (111) pre-sample monochromator was used with Cu K α_1 radiation with wavelength 1.54056 Å.

Results and discussion

Products of homopolymerisation of epoxystearic acid

The epoxidation of oleic acid was carried out as described in the experimental and below.⁴⁶ Homopolymerisation was carried out using PPD and NEt₃. The extent of epoxide ring opening was estimated using ¹H-NMR spectroscopy by dividing the integral of the signal from remaining epoxy protons over the integral from the CH₂COOH signal (equivalent to two protons) and then subtracting that value from one. Results for homopolymerisation of epoxystearic acid as a function of initiator, curing temperature and curing time (Table 1) showed that samples heated at 200 °C for 5 hours formed non-sticky solids. They were insoluble in all solvents tested and could be heated above 200 °C without melting, indicative of substantial curing. Materials made with PPD were noticeably harder and more brittle than the NEt₃ equivalent, which was more rubbery.

Increasing the temperature from 100 °C to 150 °C and extending the reaction time from 1 to 5 hours at 100 °C produced a substantial rise in epoxy ring opening. This time-temperature dependence of ring opening agrees with literature reports³⁴. As with polymers produced from diepoxides (*vide infra*), samples that were cured to a greater extent had a darker colour a trend that was much less pronounced with NEt₃ initiation which gave transparent, light orange-brown coloured materials.

Samples obtained as waxes had similar texture and softness to epoxystearic acid, reaction conditions of 100 °C for 1 hour being insufficient to completely melt the resin thus restricting mobility and hence the extent of ring opening. Samples obtained as viscous liquids appeared to become more viscous and less soluble as percentage ring opening increased, fully cured resin being completely insoluble¹⁹.

Table 1. Homopolymerisation of epoxystearic acid

Initiator	Time/h	Temp/°C	% Ring opening	Colour	Form
PPD	1	100	52	Dark brown	Soft wax
PPD	1	150	92	Dark brown	Viscous liquid
PPD	1	200	99	Dark brown	Viscous liquid
PPD	5	100	70	Dark brown	Viscous liquid
PPD	5	150	97	Dark brown	Viscous liquid
PPD	5	200	N/A	Dark brown	Brittle solid
NEt ₃	1	100	49	Pale yellow	Soft wax
NEt ₃	1	150	90	Brown-orange	Viscous liquid
NEt ₃	1	200	98	Brown-orange	Viscous liquid
NEt ₃	5	100	76	Pale yellow	Viscous liquid
NEt ₃	5	150	97	Brown-orange	Viscous liquid
NEt ₃	5	200	N/A	Brown-orange	Rubbery solid

Thus while homopolymerisation of epoxystearic acid requires fewer supplementary reagents and one less reaction step, high temperature heating periods are a disadvantage. In reports initiation by UV irradiation shows promise⁵⁴. Here, subsequent work focused on epoxidized dimers which offer a family of promising resins with considerable scope for development.

Figure 1 shows the ¹H NMR spectrum of the product of polymerization in the presence of NEt₃ at 150 °C for 5 hours.

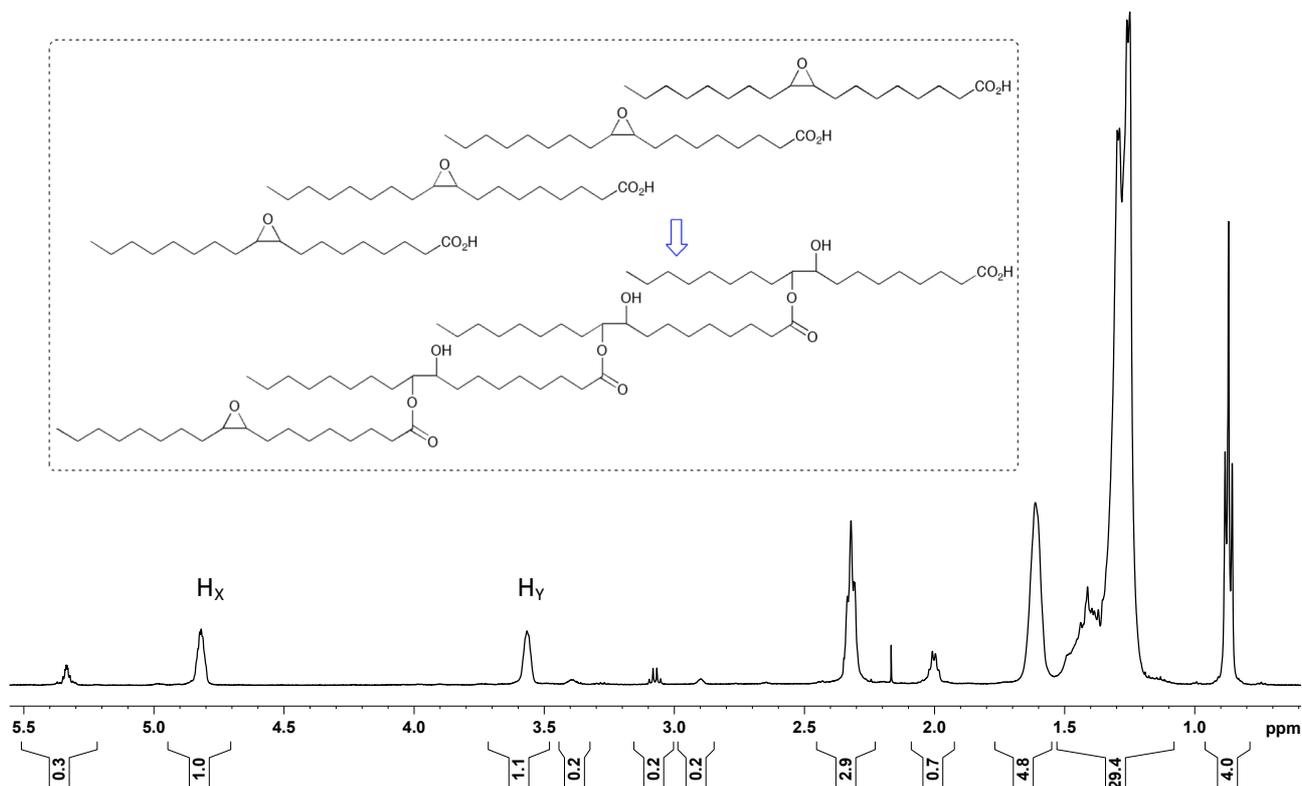
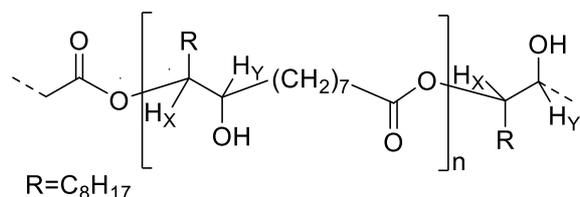


Figure 1. The ¹H NMR spectrum (in CDCl₃) of the product of polymerization of epoxystearic acid in the presence of NEt₃ at 150 °C for 5 hours. A schematic presentation of the corresponding polymerization process is also shown.

The product of polymerization shows two distinct signals at 4.82 ppm and 3.57 ppm. These are characteristic for >CH_X-O-CO- and >CH_Y-O- protons, respectively. Based on these observations, the following structure is suggested for the product of polymerization:



A schematic presentation of the corresponding polymerization process is presented in the inset of Figure 1.

Monomer synthesis: di-esters and diamide

The diesterification reaction between 1,3-propanediol and oleic acid using DCC/DMAP proceeded in good yield and the ^1H NMR spectroscopy characterisation data of the product (Figure 2) was identical to that previously reported⁴⁷. Orcyl and resorcylic dioleate were also generated using DCC/DMAP couplings and were characterised using ^1H NMR and mass spectrometry (MS). Norspermidine dioleamide⁴⁸ was prepared using standard procedures [e.g. ref 31] from oleoyl chloride, norspermidine and pyridine and was characterised by ^1H NMR and MS. Use of oleoyl chloride and direct coupling with polyamines is a more atom efficient method for amide synthesis than via Steglich couplings which produces urea waste. Future work will also focus on ester synthesis avoiding Steglich couplings. It is possible that due to the higher nucleophilicity of the secondary amine, secondary amide formation could also occur. However, the primary amines are less sterically hindered. Previous work has indicated that triamide formation requires higher reaction temperatures and that the diamide is the kinetically favoured product⁴⁹. The dioleamide product (Figure 2) was recrystallised twice: MS data of this purified material showed a peak at m/z 924, corresponding to the triamide with a relative abundance of <2% which was almost negligible compared to the dioleamide molecular ion peak at 660. The diamide has previously been investigated as a soil hydrophobic agent⁴⁸.

Some samples of orcyl and resorcylic dioleate were purified using column chromatography while for norspermidine-dioleamide, recrystallisation was used. Residual *N,N'*-dicyclohexylurea (a side-product of the DCC coupling reaction) and oleic acid could reduce the extent of polymerisation: oleic acid has only one olefin moiety per molecule and may thus induce termination. Removal of oleic acid from crude orcyl and resorcylic dioleate may be important due to the potential plasticizing effect of oleic acid.

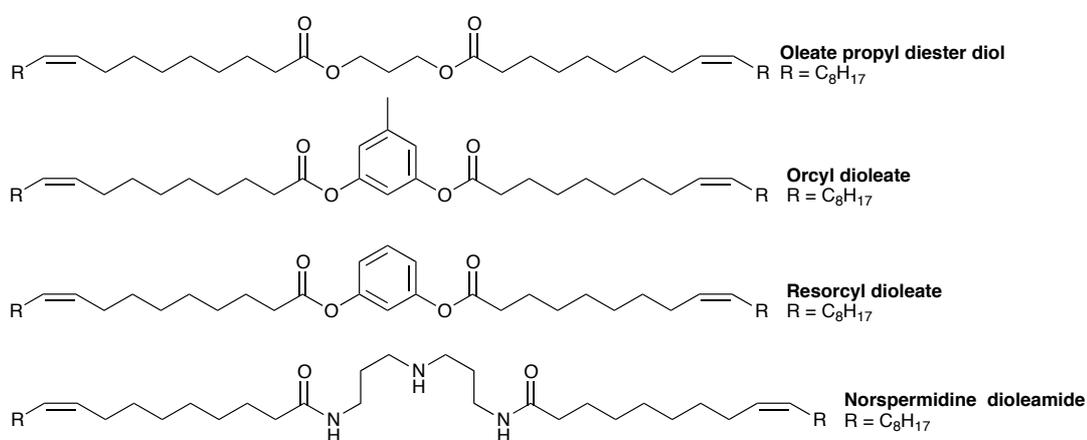


Figure 2. Di-esters and diamide synthesised

Monomer synthesis: epoxidation of oleic acid, the di-esters and diamide

Initially hydrogen peroxide was used at high temperature to carry out the epoxidation as previously reported⁵¹. The epoxy group is not strongly characterized in the infrared spectrum⁵⁵ so conversion of oleic acid and its di-ester to epoxides was monitored using ¹H NMR spectroscopy: epoxidation was indicated by disappearance of the alkene CHs at ~5.3 ppm and appearance of a peak at ~2.9 ppm which corresponded to the CH protons of the epoxy group. Oleic acid was epoxidized to give epoxide **A** (Figure 3) in high purity and 41% yield.⁵⁰ However, using hydrogen peroxide and a similar procedure, the epoxidized di-ester **B** was formed in 50% yield, and 55% purity (oleate propyl diester diol remained from analysis of the ¹H NMR spectrum). Using analogous procedures orcyl dioleate and resorcyl dioleate were fully epoxidized to give epoxides **C** and **D** in 75% and 69% yields, respectively. During epoxidation in the presence of formic acid, the hydrogen peroxide may also cleave the ester bond, however no ¹H NMR signals corresponding to the diols were observed. Formation of the epoxides was further confirmed by MS. Epoxidation of norspermidine-dioleamide to give **E** in good purity using H₂O₂ was achieved in 60% yield.

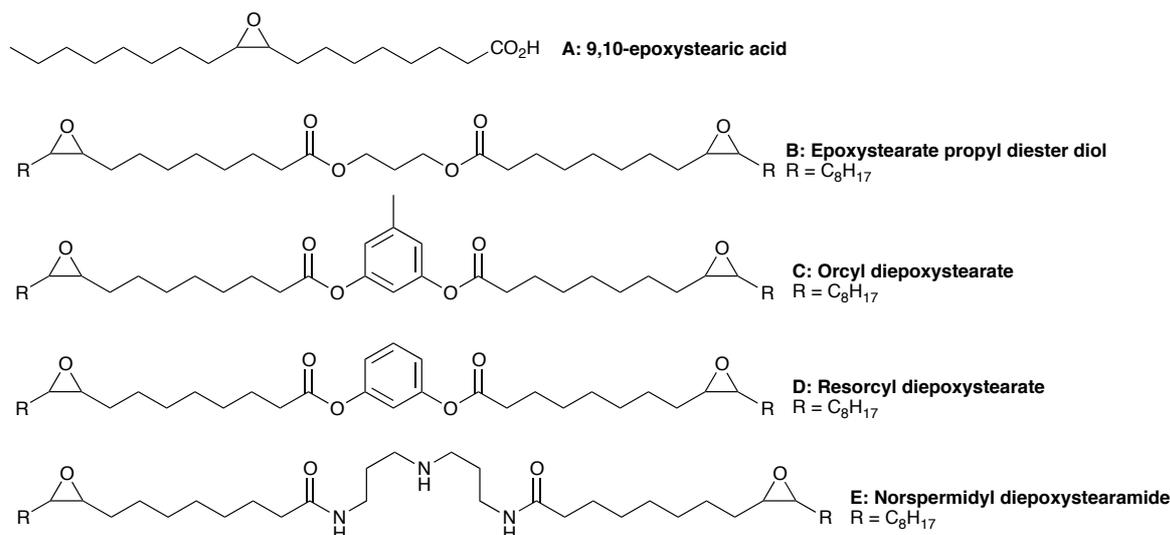


Figure 3. Epoxides synthesised

mCPBA was also employed as an alternative epoxidising agent to H₂O₂ for the orcyl and resorcyl dioleates and the reaction can be performed at ambient temperature. Epoxidation by mCPBA of the orcyl and resorcyl dioleates gave **C** and **D** in 87% and 77% yields respectively, 12% and 8% higher yields than when using hydrogen peroxide.

Anhydride curing of epoxystearic acid followed by esterification

The products of epoxidized oleates with a cyclic anhydride as curing agent are neither crosslinked¹⁵, rubber-like or highly flexible⁵¹ according to the literature. This was confirmed with epoxystearic acid **A** before using the di-esters for the reaction. Curing reactions were carried out at 165 °C for 3 hours, as in Nicolau's work¹⁵, and 200 °C for 1 hour as in Rosch's work⁵¹. It should be noted that the carboxylic acid group can also react with the anhydride leading to ring opening and subsequent polymerization.

Infrared spectra of reaction products of epoxystearic acid and cis-1,2-cyclohexanedicarboxylic anhydride under these conditions (165 °C for 3 hours/200 °C for 1 hour) were similar (Figure 4). Peaks in the region of 1735-1729 cm⁻¹ are attributed to the stretching vibrations of the C=O of the carboxylic acid group while those at 1250 and 1170 cm⁻¹ correspond to the C-O-C bonds of the ester linkages. Peaks around 3000 cm⁻¹ represent the CH₂ asymmetric and symmetric stretching vibrations.

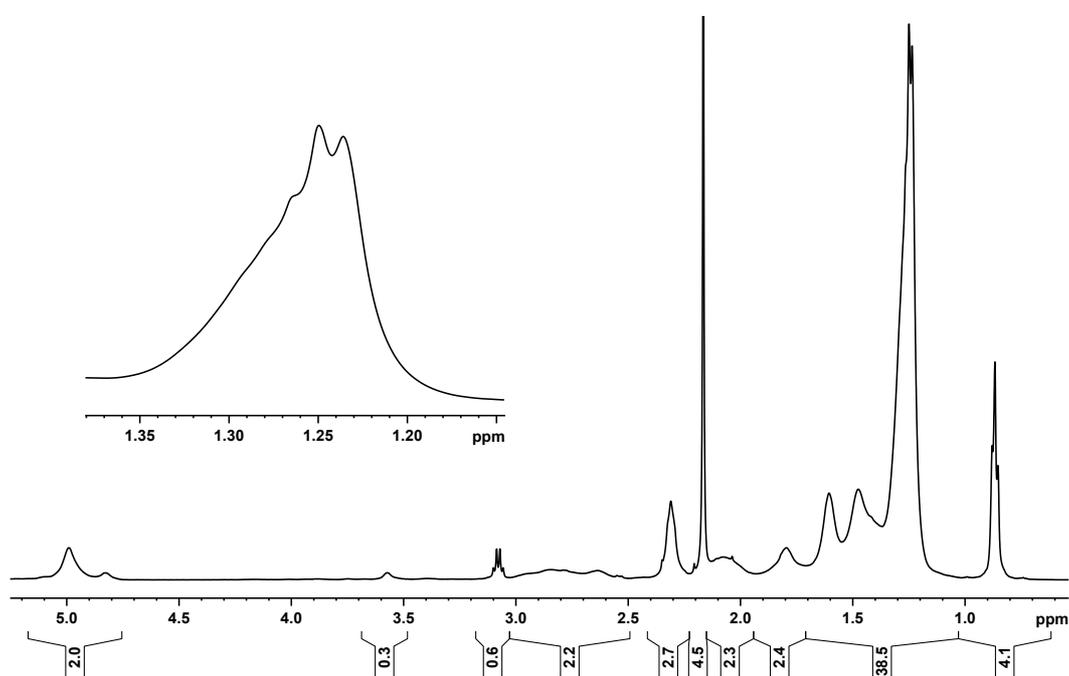
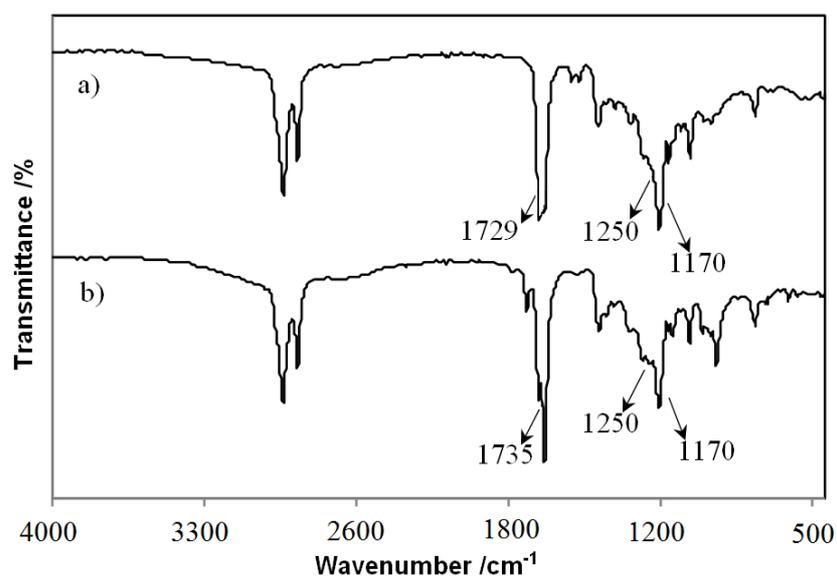


Figure 4. FT-IR of the product of the reaction of epoxystearic acid and *cis*-1,2-cyclohexanedicarboxylic anhydride from a) 165 °C for 3 h and b) 200 °C for 1 h (above) and the ^1H NMR spectrum (in CDCl_3) of the product heated at 165 °C for 3 h (below).

In the ^1H NMR spectrum of anhydride-cured products obtained at 165 °C from epoxystearic acid (Figure 4), signals at ~ 5 ppm were attributed to the H_A protons of the ester linkage formed by the incorporation of the anhydride. Three broad signals can be identified at 5.10, 4.99 and 4.83 ppm with the integral intensity ratio of approximately 1:12:2. The signals at 4.83 and 3.57 ppm are due to the homopolymer of the epoxystearic acid (Figure 1). The smallest signal at 5.10 ppm may be

due to the end-group $>CH_A N^+$ or $>CH_A O$ protons, although further studies are needed in order to verify the origin of this signal. Broad overlapping signals between 2.5-3 ppm are assigned to the CH protons of the 1,2-substituted cyclohexane fragment in the anhydride-cured polymer, although a fraction of these is due to unopened oxirane protons at 2.90 ppm. The other signals are consistent with the material reported by Nicolau¹⁵.

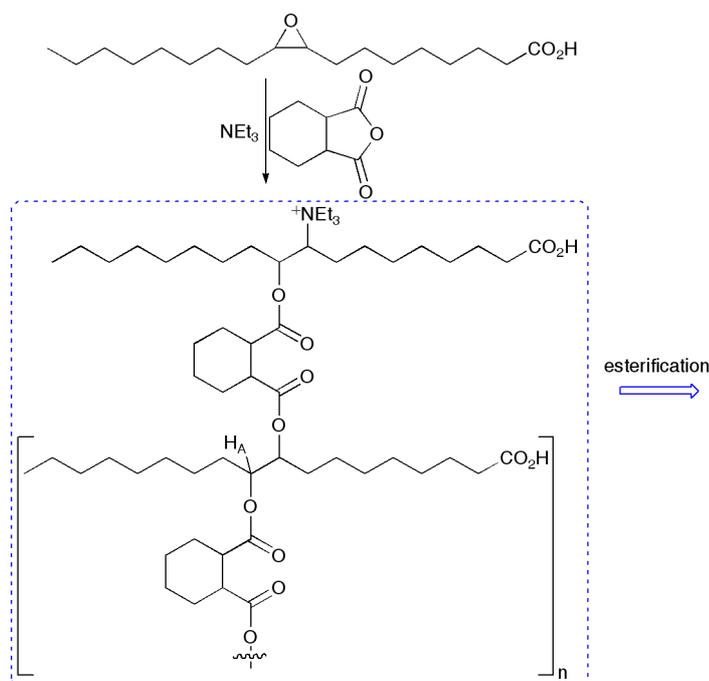


Figure 5. The scheme of the reaction of epoxystearic acid with anhydride (n = degree of polymerization).

The previously suggested scheme¹⁵ of anhydride curing reaction from oleic acid is shown in Figure and is in agreement with our results described above, although the presence of the $^+NEt_3$ end group may need further verification as the its replacement by the hydroxyl group cannot be ruled out. The products were soluble in chloroform, DMSO, acetone, toluene and DMF, indicating they were not crosslinked.

It was decided to investigate whether the acid groups could be esterified after the epoxidation step, effectively giving a diol the role of curing agent. The products of epoxidized oleic acid and anhydride obtained at 165 °C (being un-crosslinked according to 1H NMR and FT-IR), were then esterified at 160 °C with titanium (VI) *n*-butoxide⁵³ using 3 different diols: resorcinol, orcinol and 1,3-propanediol, essentially making esterification the last, rather than the first step. When 1,3-propanediol was used, there was no change in the waxy appearance of the product of epoxidized oleic acid and anhydride. When orcinol was employed, upon cooling the product solidified after 1 hour at ambient temperature. During the esterification reaction with resorcinol, the product solidified after 7 minutes producing a dark-brown polymer.

After orcinol esterification, no solubility was observed in toluene but the material was partially soluble in CDCl_3 and DMSO. For the reaction product from resorcinol, there was no detectable solubility in these solvents or in toluene after 1 week. The absence of solubility suggested that crosslinking of the polymer occurred when esterified. Thus the pathway of using a diol to crosslink an epoxystearic acid previously dimerised by anhydride emerges as a route to a family of thermosetting polymers much deserving of further development.

Figure 6 shows the solid-state ^{13}C CPMAS TOSS NMR spectrum for resorcinol esterified resin which was consistent with the conjugation of resorcinol to the polymer. In the area of carboxylic carbons between 166-183 ppm, the relatively strong signal at 174 ppm can be assigned to carboxylic carbons attached to the cyclohexane ring (e.g., 173.9 ppm in dimethyl cyclohexane-1,2-dicarboxylate,⁵⁶ while the signal at 167 ppm is characteristic for carboxylic carbons attached to the benzene ring.⁵⁷ The signal at 183 ppm is due to the acid CO_2H carbon attached to the alkyl chain (e.g., 180.3 ppm in octanoic acid⁵⁸), which is attributed to unesterified CO_2H groups in the resorcinol esterified resin. The signal due to the resorcylic quaternary C-O carbons is observed at 152-160 ppm, with the signal maximum at 158 ppm. As confirmed by the CPMAS TOSS NQS experiments, other signals due to the protonated aromatic resorcylic carbons are at ~129 ppm (meta to aryl C-O) and ~108 ppm (ortho/para to aryl C-O). Aliphatic $>\text{CH-O}$ ^{13}C NMR signals can be observed at 74.3 ppm. The relatively small signals at 64.9 and 19.9 ppm are assigned to the $-\text{CH}_2\text{O}-$ and Me-CH_2- carbons of titanium (IV) *n*-butoxide, respectively.⁵⁹ The cyclohexyl CH signals are observed at 45 ppm and remaining aliphatic carbons are at ~14-35 ppm.

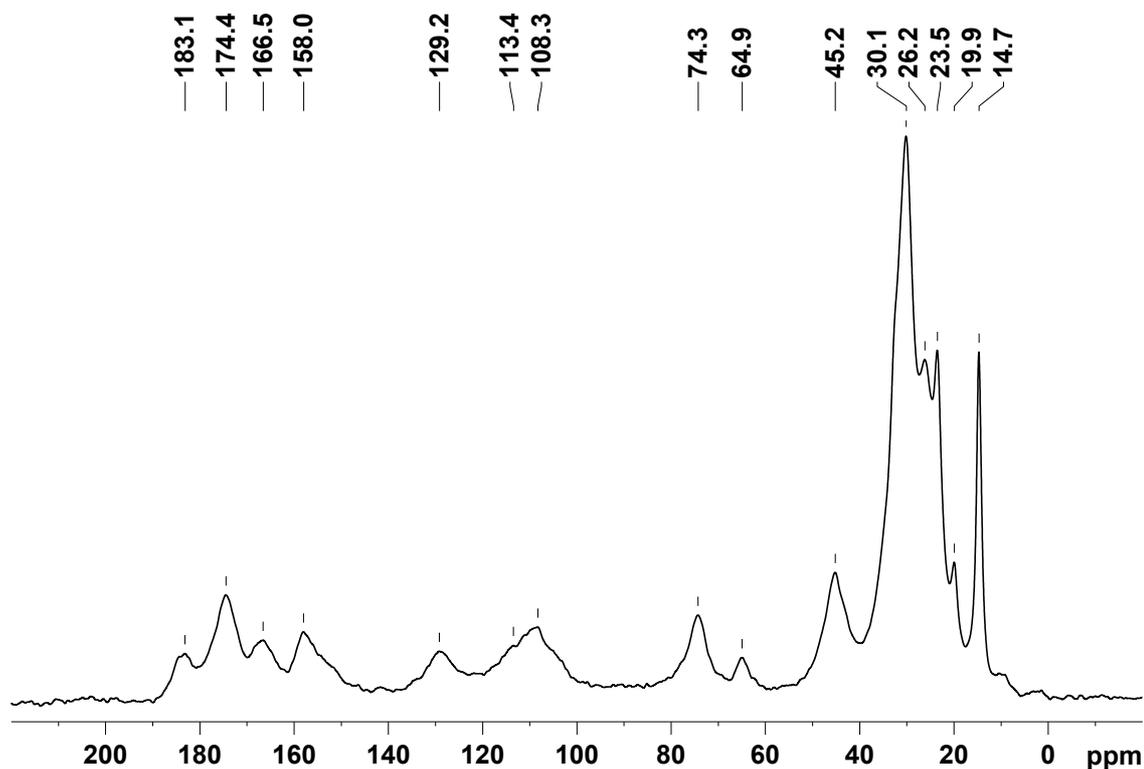


Figure 6. The solid state CPMAS TOSS ¹³C NMR spectrum for epoxystearic acid reacted with cis-1,2-cyclohexanedicarboxylic anhydride and then esterified with resorcinol.

Amine curing of epoxy distearates.

Initially, attempts were made to polymerize diepoxystearates (Figure 3: epoxides **B,C** and **D**) at room temperature using diethylenetriamine (DET) and *p*-phenylenediamine (PPD) curing agents (Figure 7) with a 1:1 ratio of the amine and epoxy group.

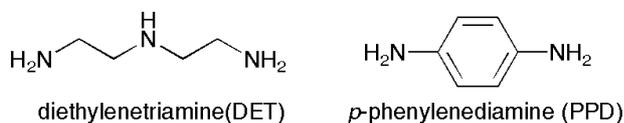


Figure 7. Amine curing agents

Secondary and primary amines are capable of forming a linkage to one and two epoxy groups respectively. Hence one DET monomer can in principle link to five epoxy groups and one PPD monomer can link four epoxy groups. PPD as an aromatic amine, typically produces cured resins with high chemical and thermal resistance properties but tends to require long cure cycles at high temperatures. The FTIR spectra of the products were similar. Absorptions in the region of 3350-

3400 cm^{-1} can be attributed to the N-H bond vibration of the amine group from the curing agents, indicating that there is residual unreacted amine. The broadening of the signal in the region of 3200-3570 cm^{-1} could also be ascribed to the stretching vibrations of -OH groups from the opening of the oxirane ring in the curing reaction.

In the room temperature cured materials the ^1H NMR spectra showed weak signals from residual epoxy group protons even when all curing agent appeared to have been consumed; products were all in the form of waxes and were soluble in chloroform and acetone.

Epoxidized resorcinol (epoxide **D**) and 1,3- propanediol diesters of oleic acid cured with PPD and DET which had not been subjected to column purification were then heated at 150 $^\circ\text{C}$ for 16 hours. They formed hard solids which were insoluble in chloroform. After two weeks with intermittent shaking a slight yellow discolouration was seen suggestive of leaching of minor amounts of low molecular weight material but the bulk remained as a robust solid.

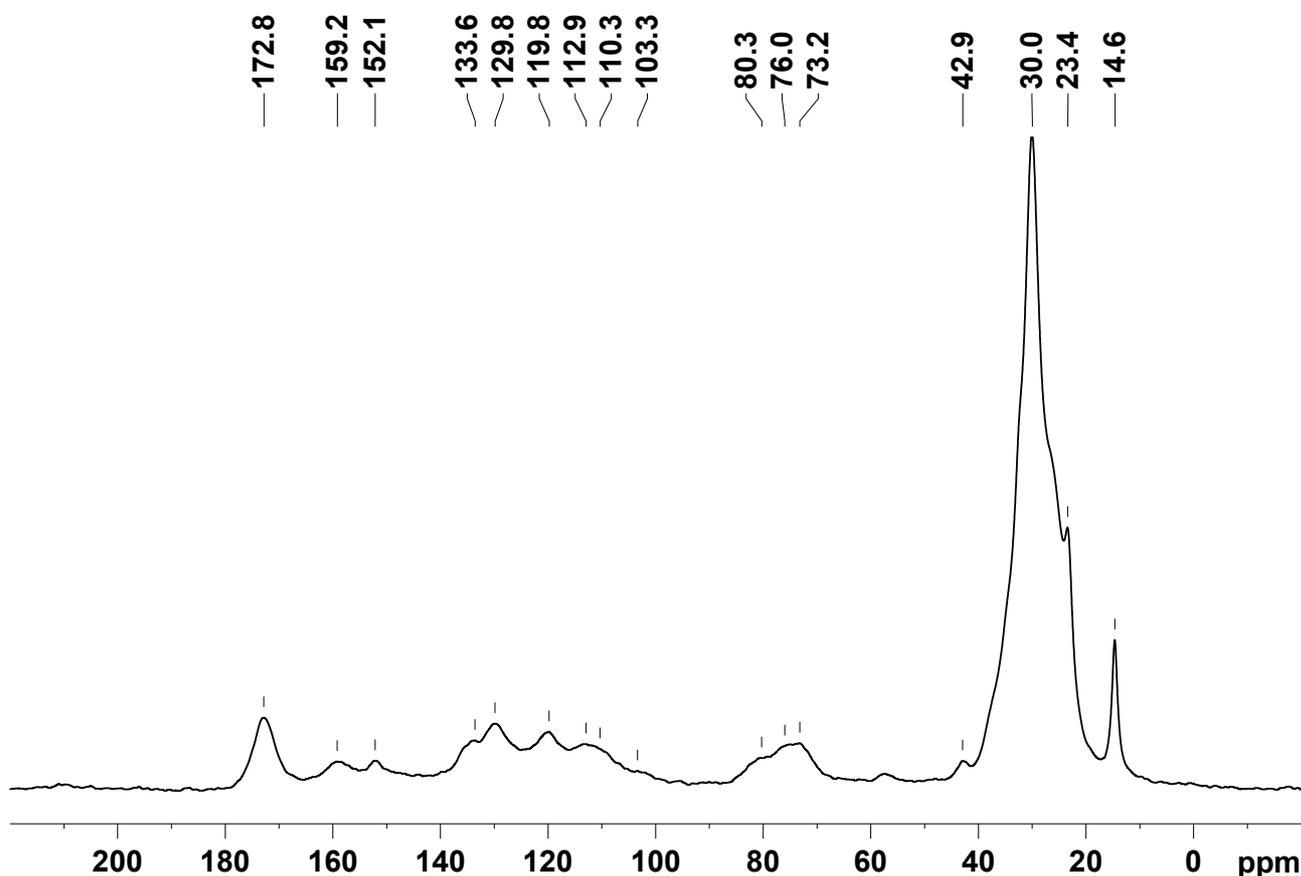


Figure 8. The solid state CPMAS TOSS ^{13}C NMR spectrum of epoxide **D** cured with PPD.

The solid-state ^{13}C NMR spectrum (Figure 8) shows only a small signal at 58 ppm, which can be attributed to either the residual oxirane carbon (expected at 54-57 ppm^{15,60}) or to the end group >CH-N carbon. This confirms that the majority (if not all) of epoxy rings have been opened. As confirmed by ^{13}C CPMAS NQS TOSS spectra, aromatic C-N and C-O peaks are at 144-162 ppm

and the ester remains intact with a carbonyl signal at 173 ppm. The aromatic CH carbons are at 102-136 ppm and the aliphatic >CH-O carbons are at 68-86 ppm. The remaining aliphatic methylene carbons are at 21-44 ppm and the methyl carbons are at 15 ppm.

The orcinol-diepoxy (epoxide **C**) which had not been subjected to column purification was cured with PPD at 150 °C for 16 hours and produced a hard solid that was insoluble in chloroform after 2 weeks indicating that the purification step is not essential for creating a strong solid.

Similarly when column-purified epoxides **B-E** were subjected to high temperature curing with PPD by heating for 16 hours at 150 °C, hard solids were formed. These conditions were effective in curing these epoxy resins whereas lower temperatures or heating times yielded samples that were incompletely solidified. All PPD-cured diepoxy resins produced insoluble black solids which were highly resistant to scratching or indentation. After initial curing, the samples were tested at 200 °C where no significant signs of melting or alteration of their characteristic features were observed suggesting they had formed thermosets. These observations imply that these samples had all formed extensively cured epoxy resins. Once the resins had cured they appeared strong and highly resistant to removal from the glass sample tube. These properties suggest that the polymers have the potential for applications as adhesives with high temperature resistance. Initially, the epoxy resins were highly transparent, colourless or pale yellow oils. On addition of PPD the mixtures turned orange-brown colour and became slightly cloudy becoming increasingly dark in colour as the reactions progressed. The final products were black and opaque.

PPD appears to be a highly effective hardener though unfortunately it does not occur naturally. Preliminary tests were carried out into the hardening efficacy of norspermidine as curing agent however these yielded viscous liquids as products. The molecular structure of DET is much shorter overall than norspermidine and PPD, which also cures well, is also shorter and more rigid than DET given its central aromatic ring. Possibly the terminal amine “heads” find it easier to cross-link two epoxy-monomers when the monomers are not required to be so widely spaced.

Interactions with Smectite Clay

The swelling of clays by polymer precursors indicates the possibility of preparing nanocomposites by intercalation followed by *in situ* curing and was assessed by change of the basal plane spacing (d_{001}) of pristine clay and four modified clays using XRD. Methanol was used as solvent to introduce organic species so a control trace is shown in Figure 9 for the effect of methanol alone. The (001) peak at 7.1° (12.5 Å) for the untreated clay is shifted slightly to 7.2° (12.2 Å) suggesting methanol removes some gallery water. The methanol-MMT trace therefore offers a control for all subsequent experiments: methanol being used as solvent in each case.

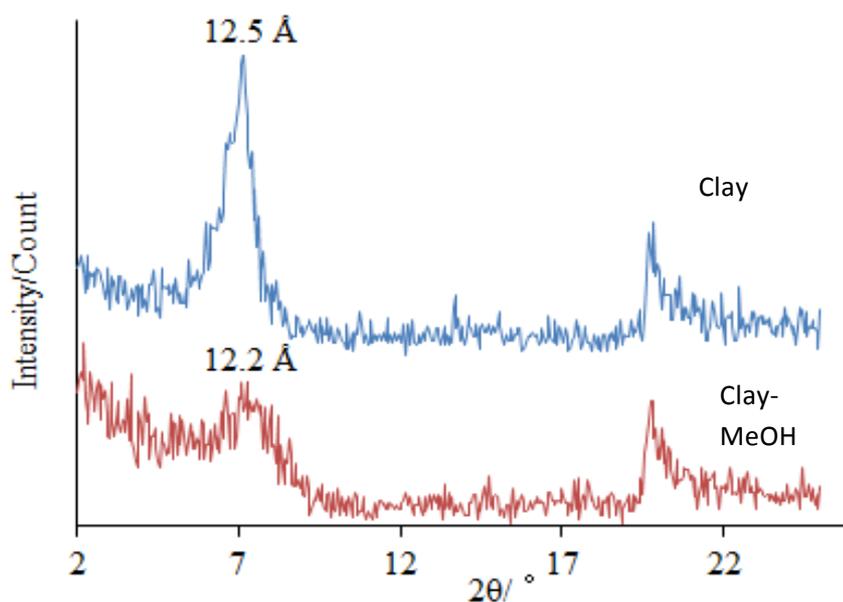


Figure 8. X-ray diffraction patterns of clay as-received and clay dispersed in methanol and then dried (Traces have been shifted on the ordinate for clarity).

Reagent oleic acid dissolved in methanol had no significant effect on d_{001} after 86 ks (1 day), 2.6 Ms (1 month), or 7.8 Ms (3 months). Similarly, the epoxystearic acid produced a single peak at 12.5 Å after 2.6 Ms (1 month) immersion (Figure 10). It appears that intercalation of these precursors does not provide a pathway to nanocomposite formation with untreated montmorillonite.

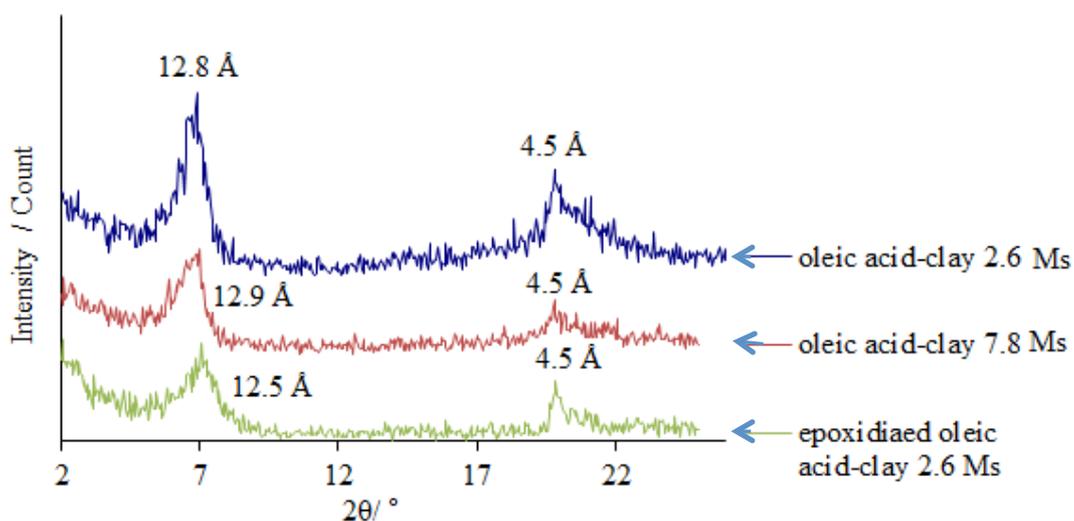


Figure 10. X-ray diffraction patterns of clay treated with oleic acid (1 month and 3 months) and epoxystearic acid (1 month) using methanol as solvent. (Traces have been shifted on the ordinate for clarity).

The XRD traces for the clays treated with epoxystearic oleic acid showed that for PPD modified clay, no intercalation occurred and d_{001} increased by only 0.2 Å. The d_{001} for ALA modified clay actually decreased by 1.5 Å, suggesting that methanol extraction of the aminolauric acid took place. The DET modified clay also did not accept the epoxystearic acid.

Figure 11 shows XRD patterns of the commercially available Cloisite® 10A with oleic acid. This organophilic clay which is treated with a benzyl(hydrogenated tallow alkyl)dimethyl salt giving it an initially higher basal spacing is generally regarded as a receptive host for polymers⁴⁴. Oleic acid increased d_{001} from 19.2 Å to 23.2 Å, an expansion of 21% and a new peak appeared at 15.8 Å.

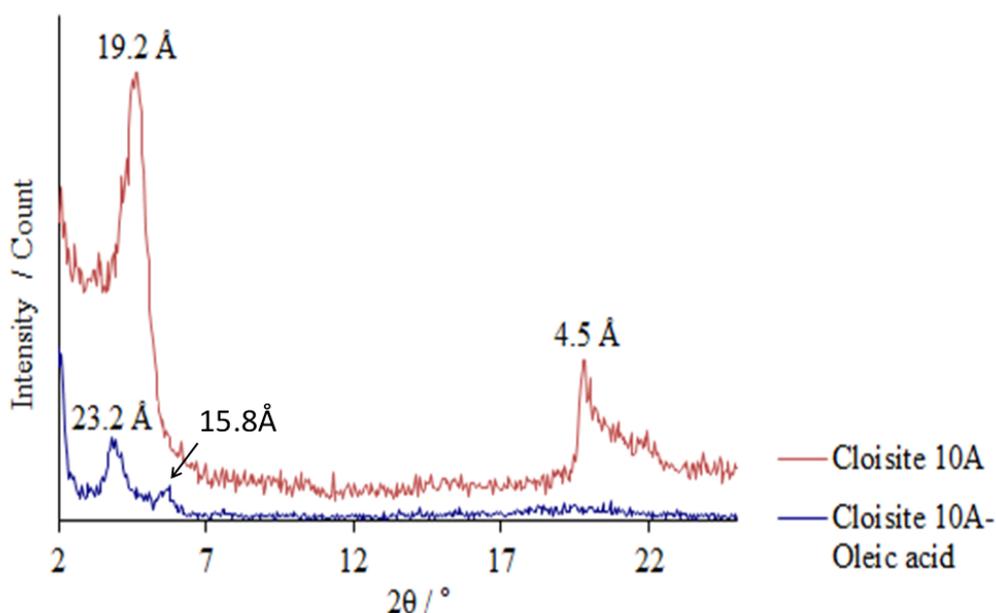


Figure 11. X-ray diffraction patterns of organoclay with oleic acid using methanol as solvent. (Traces have been shifted on the ordinate for clarity).

The use of untreated clay is preferred for an industrial procedure since no additional step is needed and the cost of feedstock is lower but these advantages must be set against the mechanical and barrier properties of the resulting composite. This work indicates that the polymer precursors do not intercalate from solution in untreated clay and even in clay that has been pretreated to make it compatible with epoxy resins. The commercial clay Cloisite 10A with an initially much expanded basal plane does host oleic acid in the galleries and provides a direction to epoxy-clay nanocomposites with low petroleum input. In support of this conjecture, an epoxidized soybean oil

has been shown to produce intercalated nanocomposites with 5 wt.% of a comparable organoclay that offers 3.5 times modulus and twice the tensile strength without loss of elongation at break.⁶¹

Conclusions

This work sets out several alternatives to the homopolymerization of epoxystearic acid so that oleic acid from seed waste can be incorporated into materials manufacture. Oleic acid was esterified with propanediol, orcinol and resorcinol to provide a precursor with two double bonds which were then epoxidized using hydrogen peroxide or *meta*-chloroperbenzoic acid. Similarly a dioleamide was prepared with norspermidine and epoxidized. These precursors were cured at 150 °C using diethylenetriamine or *p*-phenylenediamine to produce hard insoluble resins. Furthermore, the products of epoxystearic acid and anhydride obtained at 165 °C which were not crosslinked could then be esterified using resorcinol or orcinol so that esterification became the last step. While neither oleic acid nor epoxystearic acid intercalated into unmodified montmorillonite, an organoclay was found that acted as a host for oleic acid and this opens the possibility for *in situ* intercalation so that a new family of epoxy nanocomposites could be prepared with considerably reduced petroleum input.

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