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# Epoxy resin blends and composites from waste vegetable oil

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## Abstract

Thermosets and composites were prepared from blends of epoxidized waste vegetable oils and diglycidylether of bisphenol-A to investigate this material as an alternative triglyceride source for oleochemistry. Purifications were developed to remove impurities derived from thermal degradation in the frying process and different epoxidation methodologies were investigated. Effects of epoxidized vegetable oil content (up to 30 wt %) and origin on the tensile properties were studied and revealed that purified waste oils performed similarly to neat oil in contents up to 10 wt %, proving that this strategy does not compromise tensile properties when waste oils are used in suitable proportions. Furthermore, a more prominent plasticizing effect was observed when more than 15 wt% of bio-based resin was used as confirmed by DMA. Composites were prepared with recycled carbon fibres (up to 30 wt %) and thermosets with 10 wt% of bio-based epoxy resins, significantly improving the mechanical properties.

Keywords: Biopolymers, Thermosetting resins, Material testing, Vegetable oil.

# 1. Introduction

Vegetable oils (VO) gained prominence in the last decade as an alternative bio-based platform for several technological applications. Characteristics such as its renewability, price and considerable availability all over the globe categorizes VOs as a key component for the future of green materials.[1,2] Currently, epoxidation represents the most commercially important transformation of VOs to produce adhesives, plasticizers and bio-based epoxy resins.[3-5] However, particularly with epoxy resins, structural characteristics of the triglycerides such as the long aliphatic chain directly affect the structural properties of the material. Typically, these resins originate thermoset polymers with inferior mechanical performance when compared to commercial resins based on diglycidyl ether of bisphenol A (DGEBA).[6]

To overcome these drawbacks, partially bio-based blends of epoxidized vegetable oils (EVOs) with DGEBA have been extensively explored to produce materials allying bio-based content and enhanced mechanical properties. The production of DGEBA/epoxidised soybean oil (ESO) blends cured in the presence of methyl nadic anhydride (MNA) and phthalic anhydride (PA) are reported and the bio-based materials increased the impact properties and adhesive strength.[7,8] Similar systems based on different EVOs derived from castor oil [9], crambe oil and rapeseed oil [10] were also investigated and proved both excellent thermal stability and improved toughness in comparison to DGEBA analogous. In these systems, authors could detected the influence of bio-based content on properties such as peak maximum temperature, cure activation energy, initial decomposition temperature and temperature of maximum degradation rate.[9,10] Similarly, DGEBF blends with epoxidised linseed and soybean oil were also reported and promoted great improvements in Izod strength, fracture strength and tensile properties.[11,12]

Although the literature presents a collection of studies in this topic, cost has restricted the industrial application of these materials as they remain uncompetitive in comparison to the petroleum-based resins.[13] Moreover, the use of edible oil for engineering proposes rise discussions about the ethical use of land, the exclusion of VOs from the food chain and how it can negatively affect the price of staple markets.[14] In this regard, the production of bio-based materials from non-edible sources have been chased in a number of works and in particular castor oil has been demonstrating applicability in a range of areas.[15,16]

A promising yet underexplored alternative source of triglycerides is waste vegetable oils (WVO), emerging as candidate to satisfy the need for low cost materials that also does not compete as feedstock.

Currently, technological use of WVO is limited to its conversion into methyl esters and use as biodiesel [17], strategy which proven to be a successful alternative to reduce cost of the final materials in comparison to the use of neat oil sources.[18] Furthermore, technological valorisation of WVO also addresses a the serious environmental problem associated to incorrect disposal that contributes to severely compromising aquatic life (as a result of oxygen depletion).[19,20] In the EU, it is estimated that over 700 000 tonnes of WVO are generated yearly whilst in the Chinese market this scale jumps to 4.5 million tonnes per year, representing a large scale issue that urges to be addressed [21]

The biggest challenge to implement WVOs as a manufacturing platform is their heterogeneity as consequence of the reactions caused by the frying process. The combination of heat, air and water induces a series of interconnecting transformations that generate a complex mixture of by-products.[22,23] Hydrolysis of the ester bonds that link the fatty acid chains to the glycerol backbone forms free fatty acids, mono- and diglycerides. Thermal oxidation reactions are triggered by the formation of allylic radicals due to the relatively low bond energy between the hydrogen and the allylic carbon, which causes differences in oxidative stability of stearic, oleic, linoleic and linolenic acid derivatives.[23] Similarly, polymerization mechanisms are initiated by allylic radicals and produces dimers either through the combination of allylic radicals through the creation of a C-C bond or via C-O linkages by the combination of allyl and alkoxy radicals.[24] These products can repeatedly react and combine to create higher molecular weight species from trimers to polymers that deeply affect the physical and chemical characteristics of the oil.[25]

In this work, the incorporation of epoxidized WVO in DGEBA formulations was studied to evaluate these materials as alternative sources of triglycerides for the production of thermoset polymers. Purification methodologies were developed targeting the elimination/reduction of by-products formed during frying and WVO (and analogous) were epoxidized via different methodologies to comprehend factors that could affect the creation of oxirane rings, characteristic that is crucial to obtain materials with satisfactory mechanical properties. Later, milled recycled carbon fibres (MCF) were added to the blends to promote the recovery of mechanical properties and further reinforcement.

## 2. Experimental

## 2.1 General considerations

Virgin and waste vegetable oil samples (blend of rapeseed/palm oil) used as frying medium for 4 days were collected from food outlets at University of Warwick, Coventry, UK. Hydrogen peroxide (30 % v/v), m-chloroperbenzoic acid (mCBPA, 77 wt %), toluene (puriss. p.a. >99.7 %), methylene chloride CHROMASOLV Plus), were supplied by Sigma-Aldrich. Activated carbon, $HNO_3$, $MgSO_4$ were supplied by VWR International. Super Sap CLR® was used as the epoxy part A (DGEBA, Entropy

Resins, United States) and a part B of hardener (mixture of isophorone diamine and 1,3-benzenedimethanamine, Entropy Resins, United States). Recycled carbon fibres (Carbiso™ MF) were supplied by ELG Carbon Fibre Ltd. with nominal average diameter of 7.5 μm and average length of 80 μm. All chemicals, with the exception of the WVO samples were used as received.

Infrared spectra (ATR-FTIR; Cary Tensor 27) were obtained in a range of 4000–500 cm$^{-1}$, accumulating 24 scans with a resolution of 4 cm$^{-1}$. $^1$H NMR spectra were recorded on Bruker spectrometers HD Avance III 300 MHz & Bruker Avance III 400 MHz, operating at 300.129 MHz and 400.047 MHz, respectively. Dynamic mechanical analysis (DMA) was carried using a Triton Tritec Dynamic Mechanical Thermal Analyser in the dual cantilever bending mode with oscillatory frequency of 1.0 Hz, from -20 to 120 at heating rate of 2 ºC min$^{-1}$ and displacement of 0.02 mm. Specimens were in rectangular form of nominal size of 1.5 x 5 x 24 mm. Glass transition temperature ($T_g$) was defined from tan δ versus temperature curve as the maximum tan δ. Weight-loss curves were measured by thermogravimetric analysis (TGA) using a Mettler Toledo TGA 1 STAR$^e$ System programmed to heat the samples from 25 to 600 °C, heating rate of 10 ºC min$^{-1}$ under $N_2$ flow of 100 mL min$^{-1}$. Curing behaviour were analysed by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 1 STAR$^e$ System programmed in dynamic mode to heat samples from 25 to 350 °C, heating rate of 10 ºC min$^{-1}$ under $N_2$ flow of 100 mL min$^{-1}$. Tensile tests were carried out in a test machine (Instron 30 kN) with tests samples in a scaled version (50 %) of the ASTM D638, test velocity of 2 mm min$^{-1}$. Mechanical parameters were calculated based on the average of a minimum of seven specimens.

### 2.2 Purification of WVO
### 2.2.1 Single extraction.
WVO (50 mL) was filtered to remove solid impurities and subsequently diluted in of $CH_2Cl_2$ (25 mL) to reduce the viscosity. The solution was washed with saturated solution of NaCl (25 mL) at 60 °C .The mixture was separated and the organic phase was dried over $MgSO_4$, filtered and the solvent was removed using a rotatory evaporator. A clear brown oil was obtained (90% yield).[26]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.26 (2H, m, C$H$=C$H$), 5.26–5.20 (1H, m, C$H$O), 4.29 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 4.3 Hz, C$H$HO), 4.10 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.9 Hz, CH$H$O), 2.77 (2H, dt, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ 5.9 Hz , CH$_2$C$H$=), 2.30 (6H, t, $^3J_{HH}$ = 7.5 Hz, OCC$H_2$CH$_2$), 2.14 – 1.94 (2H, m, C$H_2$CH=CH), 1.70–1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, m, C$H_3$). FTIR: $\nu_{max}$ (cm$^{-1}$) 3009 (C–H $cis$ double bond), 2947 (CH$_3$), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 722 (CH$_2$).

## 2.2.2 Multiple extraction.

WVO (50 mL) was filtrated to remove solid impurities and subsequently diluted in $CH_2Cl_2$ (25 mL) to reduce the viscosity. The solution was washed with of saturated solution of NaCl (25 mL) at 60 °C. The mixture was left until phase separation, the organic phase was collected and the procedure repeated more four times. The crude oil dried over $MgSO_4$, filtered to remove the drying agent and the solvent was removed using a rotatory evaporator. A clear brown oil was obtained (84 % yield).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.26 (2H, m, C$H$=C$H$), 5.26–5.20 (1H, m, C$H$O), 4.29 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 4.4 Hz, C$H$HO), 4.10 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.9 Hz, CH$H$O), 2.77 (2H, dt, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 5.9 Hz , C$H_2$CH=), 2.30 (6H, t, $^3J_{HH}$ = 7.5 Hz, OCC$H_2$CH$_2$), 2.14 – 1.94 (2H, m, C$H_2$CH=CH), 1.70–1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, m, C$H_3$). FTIR: $\nu_{max}$ (cm$^{-1}$) 3009 (C–H *cis* double bond), 2947 (CH$_3$), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 723 (CH$_2$).

## 2.2.3 Purification with activated carbon

Activated carbon (5 g) was added in a beaker with concentrated HNO$_3$ solution (10 mL, 70%) at 60°C and stirred for 1 h. The mixture was filtered and the solid washed with water until the pH of the washed solution reached 7. The resulting black solid was left drying for 1 h at 110 °C in an oven with a yield of 86 %. Chemically-modified activated carbon (3 g) was added to WVO (50 mL) in a round bottom flask and maintained under stirring for 24 h at 50 °C. The mixture was subsequently filtered to separate the activated carbon from the purified oil, resulting in a brownish oil (62 % yield). [27]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.25 (2H, m, C$H$=C$H$), 5.26–5.19 (1H, m, C$H$O), 4.29 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 4.4 Hz, C$H$HO), 4.10 (2H, dd, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.9 Hz, CH$H$O), 2.77 (2H, dt, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 5.9 Hz, C$H_2$CH=), 2.30 (6H, t, $^3J_{HH}$= 7.5 Hz, OCC$H_2$CH$_2$), 2.14 – 1.94 (2H, m, C$H_2$CH=CH), 1.70–1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, m, C$H_3$). FTIR: $\nu_{max}$ (cm$^{-1}$) 3009 (C–H *cis* double bond), 2947 (CH$_3$), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 724 (CH$_2$). FTIR modified activated carbon: $\nu_{max}$ (cm$^{-1}$) 2928 (C-H) 1733 (~~NO$_2$~~), 1373 (NOH),

The same procedure was carried out using activated carbon without any prior modification for comparison proposes, resulting in a brownish oil with 67 % of yield. $^1$H NMR (300 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.26 (2H, m, C$H$=C$H$), 5.26–5.20 (1H, m, C$H$O), 4.29 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 4.4 Hz, CH$H$O), 4.10 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.9 Hz, C$H_2$O), 2.77 (2H, dt, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 5.9 Hz, C$H_2$CH=), 2.30 (6H, t, $^3J_{HH}$ = 7.5 Hz, OCC$H_2$CH$_2$), 2.14 – 1.94 (2H, m, C$H_2$CH=CH), 1.70–

1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, m, C$H_3$).  FTIR: $\nu_{max}$ (cm$^{-1}$) 3009 (C–H *cis* double bond), 2947 (CH$_3$), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 724 (CH$_2$).


## 2.3 Epoxidation
## 2.3.1 Epoxidation with peracetic acid

WVO (50 mL, 5.6×10$^{-2}$ mol, 1.2×10$^{-1}$ mol of double bonds, 1 equiv.) was added in a round bottom flask with toluene (25 mL), acetic acid (3.5 mL, 6.4×10$^{-2}$, 0.5 equiv.) and Amberlyst 15$^{®}$ (11 g, 22 wt % in relation to the oil content) as acidic ion-exchange resin (AIER). The mixture was kept under stirring at 60 °C for 30 min and then H$_2$O$_2$ 30 % v/v (29 mL, 2.5×10$^{-1}$ mol, 2 equivalent) was added dropwise over 30 min. The reaction was left for 6 h under these conditions, then the resulting product was filtered to remove the ion-exchange resin catalyst. The mixture was washed with solution of 5 wt % NaHCO$_3$ and 5 wt % NaCl until all acid residues were removed (as identified by the pH). The crude oil was dried over MgSO$_4$, filtered to remove the drying agent and the solvent was removed using a rotatory evaporator.[28] The product was a yellow oily solid (71 % yield).


$^1$H NMR (400 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.26 (2H, m, C$H$=C$H$), 5.26–5.20 (1H, m, C$H$O), 4.29 (2H, d, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 4.5 Hz  C$H_2$O), 4.10 (2H, dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.5 Hz, C$H_2$O), 2.90 – 3.20 (2H, m, C$H$OC$H$ epoxy), 2.30 (6H, t, $^3J_{HH}$ = 10.6 Hz, OCC$H_2$CH$_2$), 1.80 – 1.70 (2H, m, C$H_2$ adjacent to epoxy ring), 1.70–1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, t, $^3J_{HH}$ = 6.7 Hz, C$H_3$).  FTIR: $\nu_{max}$ (cm$^{-1}$) 3006 (C–H *cis* double bond), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 844 (C-O-C epoxy ring), 724 (CH$_2$).


## 2.3.2 Epoxidation with m-chloroperbenzoic acid (mCPBA)

In an ice bath (T< 25°C), WVO (25 mL, 2.8×10$^{-2}$ mol, 6×10$^{-2}$ mol of double bonds, 1 equiv.) was added in a round bottom flask and dissolved in CH$_2$Cl$_2$ (150 mL). mCPBA (17.4 g, 6.6×10$^{-2}$ mol, 1.1 equiv.) was dissolved in CH$_2$Cl$_2$ (100 mL) and slowly added (over 10 min). The reaction flask was kept at T< 25°C throughout the whole addition process. Once finished the addition, the ice bath was removed to permit the temperature to be raised to room temperature. The reaction was kept under stirring and room temperature for 1.5 h. The resulting solution was filtered to remove by-products and washed with solution of 5 wt % of Na$_2$S$_2$O$_5$ and 5 wt % of NaHCO$_3$. The resulting oil was dried over MgSO$_4$, filtered to remove the drying agent and the solvent was removed using a rotatory evaporator. The final product was a white oily solid (68 % yield).

^{1}H NMR (400 MHz, CDCl$_3$): $\delta_H$ (ppm) = 5.40 – 5.26 (2H, m, C$H$=C$H$), 5.26–5.20 (1H, m, C$H$O), 4.29 (2H, dd, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 3.0 Hz, C$H_2$O), 4.10 (2H, dd, $^2J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.9 Hz, C$H_2$O), 2.90 – 3.20 (2H, m, C$H$OC$H$ epoxy), 2.30 (6H, t, $^3J_{HH}$ = 7.2 Hz, OCC$H_2$CH$_2$), 1.80 – 1.70 (2H, m, C$H_2$ adjacent to epoxy ring), 1.70 – 1.52 (6H, m, OCOCH$_2$C$H_2$), 1.42–1.22 (56H, m, C$H_2$CH$_2$), 0.83 (9H, t, $^3J_{HH}$ = 6.8 Hz, C$H_3$). FTIR: $\nu_{max}$ (cm$^{-1}$) 3006 (C–H *cis* double bond), 2926 and 2854 (C–H), 1745 (C=O), 1099 (C–O), 844 (C-O-C epoxy ring), 722 (CH$_2$).

## 2.4 Preparation of blends and composites

Super Sap CLR® commercial resin was used as base for the production of the thermosets. A certain amount of bio-based resin was added to the commercial epoxy resin (Part A) in a beaker according to the targeted formulation in such way that the sum of both parts would be approximately 10 g. Formulations were prepared with bio-based resin contents of 0 wt %, 5 wt %, 10 wt %, 15 wt %, 20 wt % & 30 wt % with regards to the Part A and utilized epoxidized neat, waste and purified vegetable oils (total of 16 formulations). Sequentially, 47 wt % (in respect to the total weight of the mixture) of the amine hardener (Part B) was added to the solution and the blend was carefully stirred with a spatula for 2 min insuring proper infusion of the hardener into the epoxy resin and avoiding the formation of air bubbles. The resulting mixture was poured into dog bone shaped silicone moulds and left curing in room temperature for 24 h and post-cured in an over at 50 °C for 2 h.

Composites were prepared similarly and the reinforcing agent (milled recycled carbon fibres, MCF) was added after the part B was blended to the epoxy part in a weight percentage in regard to the total mass of the mixture. Formulations with 1 wt %, 5wt %, 10 wt %, 20 wt % and 30 wt % were prepared using a fixed bio-based content of purified oil at 10 wt %.

## 3.    Results and Discussion
## 3.1 Purification

As there is no literature supporting the purification of WVO specifically for the production of epoxy resins, different purification procedures were tested based on existing methodologies reported for the biodiesel area.[26,27] These procedures target the removal of highly oxidized compounds formed by the frying process (*e.g.* aldehydes) and hydrolysis products such as mono- and diglycerides. Samples were purified by extraction of polar products with water at 60 °C (single and multiple extraction) and adsorption with activated carbon and chemically modified activated carbon with nitric ions as described by Vásques *et al*.[27] This permitted the classification of the oil samples in three different categories:

neat oil, waste oil and purified waste oil. Although methodologies such as recrystallization, distillation and column chromatography are also reported in the literature for the manipulation of organic compounds, none of them proved to be satisfactory in terms of vegetable oil purification due to low efficiency and use of high temperatures/large volumes of solvent, which compromises the scalability of the procedure.[29]

^{1}H NMR analyses were used to track the presence of by-products of frying process and its sequential removal by the purification. Comparison of the spectra of neat and waste oil reveals the reduction of double bonds as detected by the reduction of resonance peaks at 1.94 – 2.14 and 5.26-5.40 ppm associated with α-allylic and allylic protons respectively.[30] Furthermore, the spectra also confirm the presence of by-products at 3.72 and 5.08 ppm associated to glycerol backbone in 1,2-diglycerides. The broadening of the double duplet between 4.00 – 4.35 ppm is due to the presence of 1,3- diglycerides and the shoulder at 4.18 ppm is assigned to 1-monoglycerides whereas minor signals at 9.75 and 9.5 ppm are specifically associated with n-alkanals, (E)-2-alkenals and (E,E)-2,4-alkadienals.[31,32]

Investigation of spectra of samples after performing the purification methods demonstrated that all methods were efficient to remove highly oxidized compounds as signals at the 9 - 10 ppm region were eliminated. However, partial removal of mono- and diglycerides evidenced by the reduction of signals at 3.72 and 4.18 ppm was exclusively identified in the purification procedures by aqueous extraction. These observations are illustrated in Figure 1. Based on these findings, the purification process based on multiple washings of the oil with water at 60 °C was elected as standard procedure for the preparation of the WVO for chemical modifications.
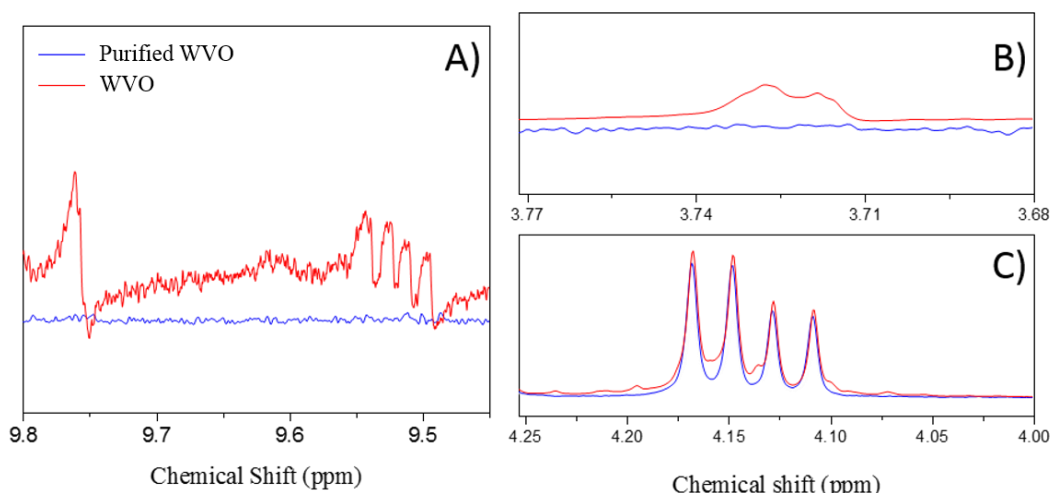


Figure 1: ^{1}H NMR signals affected by the purification procedure: a) the region of aldehydic compounds, B) and C) regions associated mono- and diglycerides.

**3.2 Epoxidation**

Samples of waste vegetable oil, neat vegetable oil and purified oil were epoxidized by methodologies based on peracids (A - acid catalyst, B ion exchange resin (AIER) catalyst) and mCPBA (C). The molar ratios of the oxygen donor and oxygen carrier, as well as the ion-exchange resin was decided according to optimization studies carried by Dinda *et al.*[33] The same procedure was also repeated without the ion-exchange resin but in the presence of 1 wt % of $H_2SO_4$ as a catalyst, however both ^{1}H NMR and FTIR signals showed no conversion when compared with the original sample.
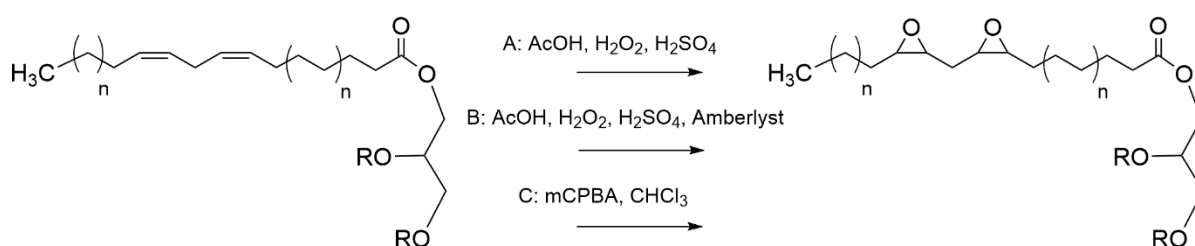


Figure 2: Schematic representation of the epoxidation methodologies explored in this study

Initial changes tracked by ATR-FTIR spectroscopy revealed the disappearance of absorbance peaks at 3006 and 1654 $cm^{-1}$ in the methodologies B and C, demonstrating the consumption double bonds at the same time that the appearance of absorption peak at 844 $cm^{-1}$ indicates the creation of oxirane rings.[34] Interestingly, ATR-FTIR spectra of samples epoxidized by the methodology A revealed that the reaction led to insignificant reduction of the double bonds and no formation of oxirane rings. This suggests that in the absence of AIER, the transference of reactive species (peracids) from the aqueous phase to the oil phase is being strictly regulated by the limited miscibility of the phases, therefore compromising the formation of the desired products.[35,36]

Epoxidation procedures were further comprehended via ^{1}H NMR. Disappearance of resonance peaks at 5.26 – 5.40 ppm (signal **a**) and 1.94 – 2.14 (signal **e**) supports FTIR data by indicating the consumption of the double bonds. New signals assigned to protons in the oxirane ring are found at 2.9 – 3.2 ppm and signals at 1.45 ppm that are associated with protons in alpha position to one oxirane whilst those at 1.75 ppm are associated to protons alpha to two oxirane rings. This collection of signals confirms the formation of the desired product as illustrated in Figure 3.  Signals **m** and **k** were exclusively found in products derived from NVO once they are specifically associated with products from highly unsaturated neat oil since they derive from bisallyic protons.
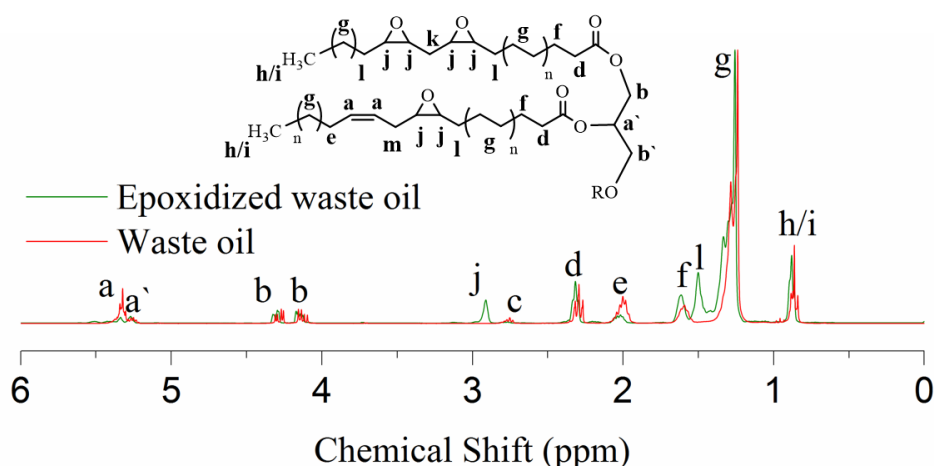
Figure 3: ^{1}H NMR spectra of waste vegetable oil before and after epoxidation (Methodology B) and assignment of the principal signals.

Table 1 presents conversion and selectivity extracted from the ^{1}H NMR spectra. Conversion is defined as the proportion between the initial number of double bonds and amount consumed by the reaction as detected through the resonance peak that represent allylic protons, whilst selectivity is the relationship between the number of oxirane rings formed in comparison to the number of double bonds initially present in the structure.[37] Difference between conversion and selectivity observed in methodology B indicates that double bonds are being partially converted to other functionalities rather than epoxy by side-reactions. These by-products are formed under the explored conditions of the methodology B due to the reactivity of the oxirane ring versus nucleophilic species.[28] However, a different behaviour is observed for Methodology C as it exhibits remarkable correlation between conversion and selectivity, indicating minimum formation of side-products as consequence of less nucleophilic species being formed. Although findings from Methodology B showed the purification has no significant impact on the reaction parameters, data from Methodology C demonstrated that the purification with aqueous extraction positively affect the formation of the desired products in both methodologies. These results suggest that species present in the WVO decrease the selective reactivity of mCPBA, although no direct observation of this effect has been done.

**3.3 Blends**

Chemically modified oils prepared by the methodology C were selected for the preparation of blends due to its higher number of oxirane rings per triglyceride unit. All samples (ranging from 5 to 30 wt % of bio-based epoxy resin) proved to be curable in the same conditions as the commercial epoxy resin and DSC analysis were performed to investigate their cure behaviour in depth. Enthalpies of curing ($\Delta H_c$) were calculated from the calorimetric curves by the integration of the exothermic curing peak and are shown in

. $\Delta H_c$ decreases (26%) in the first addition of EPVO due to the presence of less reactive epoxy groups in the epoxidized oil in comparison to the commercial resin, therefore fewer crosslinks are formed in

the structure. Values of $\Delta H_c$ remain similar along the experimental range until the transition from 20 wt % to 30 wt % of bio-based content, presenting a significant drop (32 %) in the enthalpy of curing. This represents the point where the cross-linking process is mostly affected by the presence of the less reactive sites in the chemically modified triglyceride as previously described in the literature.[5] In addition, this class of hardeners is known for not being particularly reactive towards curing of EVO-based resins as the ring-opening reaction that triggers the formation of the cross-links is driven by nucleophilic attacks are limited by the steric hindrance and the high electronic density due to the presence of vicinal aliphatic chains. Although the $\Delta H_c$ varies within the samples, the maximum curing temperature remains significantly unaffected by the oil content, which supports the fact that there bio-based resin causes no change in the curing regime.

Blends were characterised by tensile test and representative stress *versus* strain curves (Figure 4) clearly illustrates a drastic variation in the sample`s tensile behaviour as a function of the EVO content, from rigid structure in the initial formulae to solids with distinguished elongation. Figure 5A shows the comparison of the tensile Young`s moduli along the formulation range, revealing that the gradual addition of bio-based resin leads to a progressive decrease of the tensile modulus independently of origin of the used vegetable oil. Such behaviour is similar to that described in previous studies with ESO-based resins and is consequence of the reduced functionality/rigidity of the vegetable oils in comparison with the commercial formulations.[38]  The addition of 5 wt% of EPVO decreases the tensile elastic modulus from 1.5 GPa in the non-bio-based formulation to 1.2 GPa and subsequently to 1.0 GPa when the bio-based content is increased to 10 wt%. Greater decline is detected from 15 wt %, where approximately 50% of reduction is observed. This behaviour is followed by a significant change in elongation, as presented in Figure 5B. An increase of up to 900% on average elongation is detected in samples prepared with 30 wt% of EPVO in comparison to the commercial sample. As extensively discussed by Miyagawa *et al.*, these observations are consequences of the lower number of oxirane rings associated with their lower reactivity that manifests more actively from bio-based contents of 15 wt %. From this point, EVOs begin to act primarily as plasticizers when levels higher than 10 wt% are used.[11] A similar effect can be observed in the tensile strength of the polymers, as presented in Figure 5C.
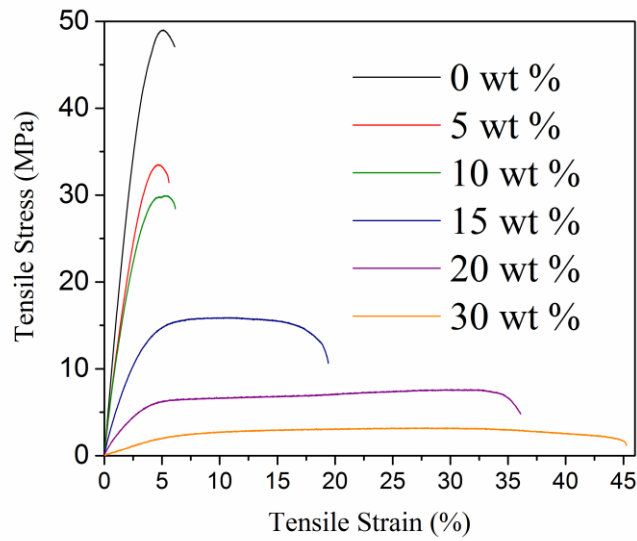
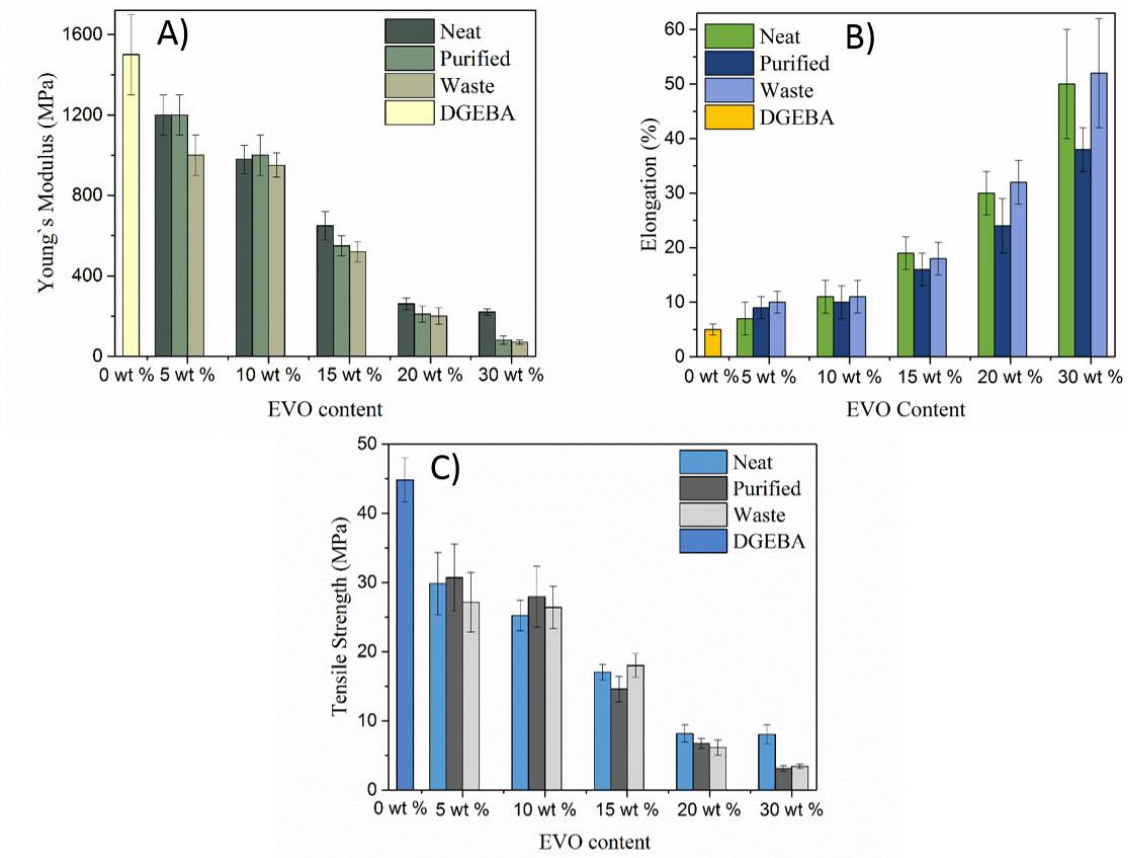Figure 4: Stress/strain curves of samples with different EPVO content.



Figure 5: A) Young`s Moduli, B) elongation at break and C) tensile strength of specimens with different EVO content and different origins.

Purified oil-derived thermosets presented equivalent tensile properties to those from neat oil when added in contents up to 10 wt %, supporting the necessity of the execution of the purification step prior to use of plant oils. From 15 wt % onwards, the average elastic modulus of EPVO derived samples start diverging from values found in ENVO-derived analogous, gradually becoming similar to those found in EWVO-based samples. This can be confirmed by the fact that, at 30 wt %, properties of EPVO-derived polymers are statistically equivalent to EWVO-based analogous. This establishes a critical point in the formulations range in which the effect of reduced reactivity becomes significant from the point of view of the tensile properties of the thermoset polymer.

DMA analysis were carried out to comprehend the plasticizing effect observed in tensile tests, in particular for EPVO-based blends. Temperature scan curves of storage modulus (E') presented in Figure 6A demonstrate the reduction of E` when the bio-based content is increased. Curves of tan δ versus temperature in the region of their maxima are shown in Figure 6B and demonstrates the shift of its maximum of the peaks to lower temperatures. Increasing the EVO content brings the $T_g$ from 56.3 °C in the non-bio-based formulation down to 27.4 °C in the sample with the highest concentration of EPVO. As all formulations share the principal chemical characteristics, the decrease in $T_g$ can be attributed to a reduced formation of cross-links between the epoxy and the hardener units due to the progressively reduction of the relative epoxy equivalent number; In addition, the increasingly presence of long aliphatic contributes to relative mobility of the network. The combination of these characteristics results in less tighten networks that concede additional mobility to the macromolecules and, ultimately, reduce the storage moduli and the $T_g$ of the polymers.[5]
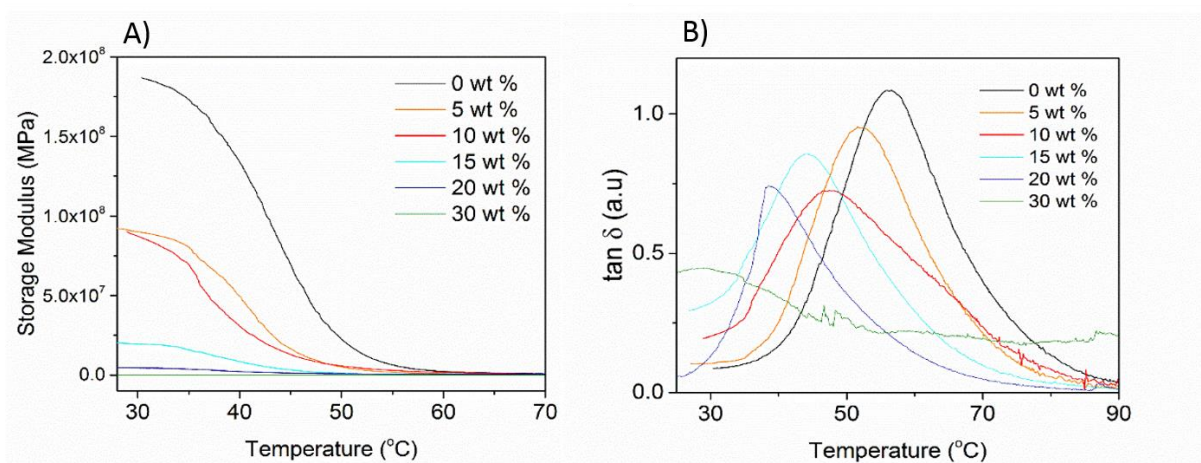
Figure 6: Curves of A) Storage modulus and B) tan δ versus temperature for samples with different EPVO oil content.

Thermogravimetric curves of EPVO-based formulations and their first derivatives are shown in Figure 7, and parameters such as temperature of thermal events degradational and maximum degradation rate ($T_{max}$) extracted from those curves are shown in Table 3. Gradual addition of EVO to the blend makes it progressively less thermally stable, which is consistent with previous observations that fewer cross-links are formed. Two main degradational events are observed in the weight-loss curve of the blends: the first event is associated with the liberation of low molecular weight species that are not connected to the network such as unreacted curing agent. This event is directly affected by the EVO content, demonstrating that less molecules of the curing agent are getting incorporated as consequence of the decreased reactivity of the system, resulting in reduced degree of curing. The latter event is the decomposition of the crosslinked network itself, which is de-bonded by the action of thermoxidative reactions.[39]
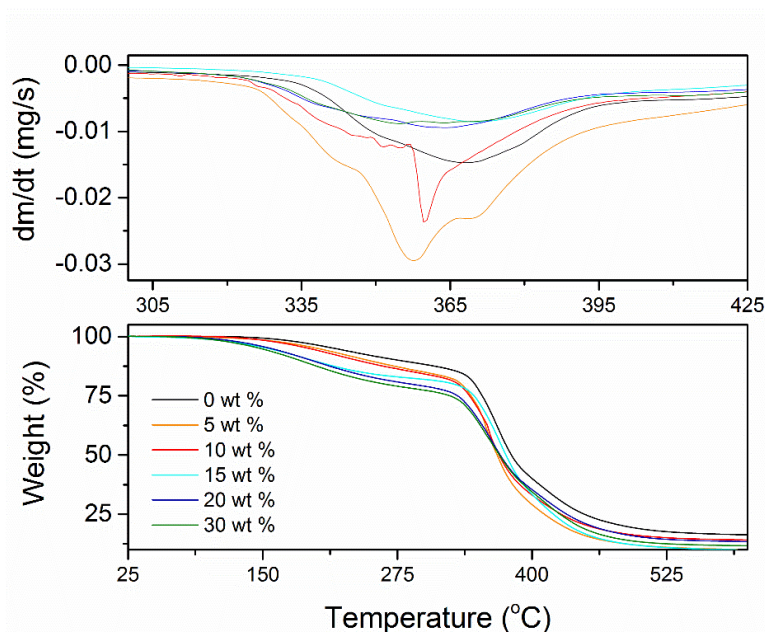


Figure 7: Thermograms of EPVO-based resins from 25 °C to 600 °C, heating rate of 10 °C min$^{-1}$, under inert atmosphere, and their respective first derivative curve.

### 3.4 Composites

The production of composites was idealised to promote the recovery of the original mechanical performance of the epoxy blends that decreased due to the addition of EVO. The formulation with 10 wt % of EPVO was elected to continue the studies as it demonstrated to be the most promising in terms of balance between neat properties and the bio-based weight fraction. In this respect, composites were

produced using MCF to manufacture materials with potentially reduced environmental impact that combines both bio-based and recycled streams.

Tensile performance of the composites was evaluated and the variation of Young's Modulus, elongation at break and tensile strength of the resulting materials are shown in Figure 8A-C. Properties are compared both with the commercial epoxy and with 10 wt % EPVO formulation. The initial properties of the commercial control reference (unreinforced) could be promptly re-achieved through the use of MCF, achieving an elastic modulus of 1.6 GPa with an increment of 5 wt %. In addition, MCF-reinforced composites continuously increased throughout the experimental range, achieving a maximum tensile modulus of 3.2 GPa in the formulation with 30 wt %. Values of elongation at the breaking point also have shown a gradual shift towards more rigid samples when MCF were added to the system as this value reduces up to a minimum 3.3 % that coincides with the 30 wt % formulation. In comparison to analogous produced from the combination of commercial DGEBA and MCF, composites based on the use of EPVO presented inferior tensile modulus; however, similar tensile strength and higher elongation at break. The difference in modulus comes from the inherently higher rigidity of the pristine DGEBA formulation in comparison to EVO.
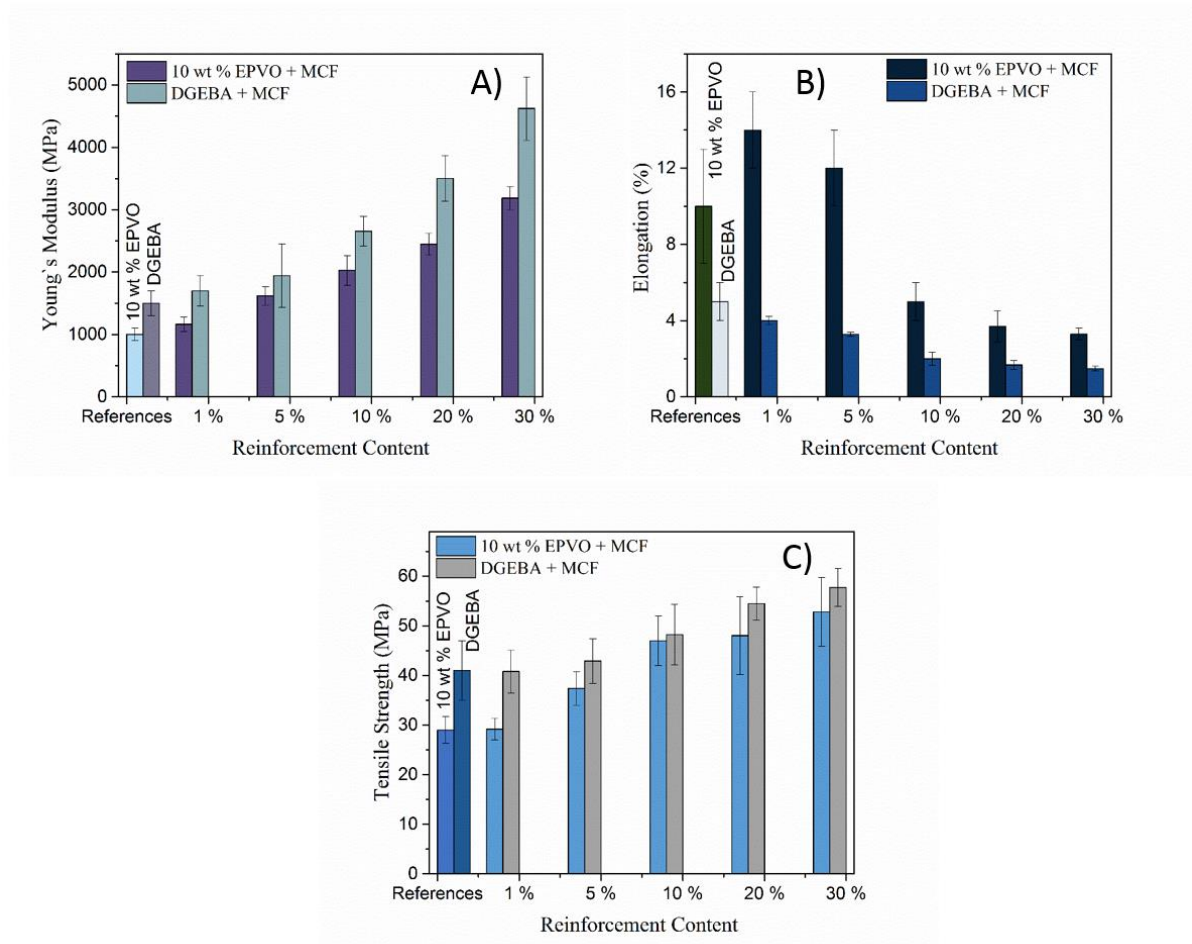


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The effect of the addition of MCF was also investigated by the optics of the dynamic-mechanical properties as presented in Figure 9. Composites prepared with MCF presented $T_g$s ranging from 49.2 °C to 51.8 °C, which represents a discreet increase in $T_g$ from original bio-based formulation (46.7 °C). Most interestingly was the noticeable increase in storage modulus of the materials with the addition of MCF, which again demonstrates the improvement of properties when the reinforcement is added.
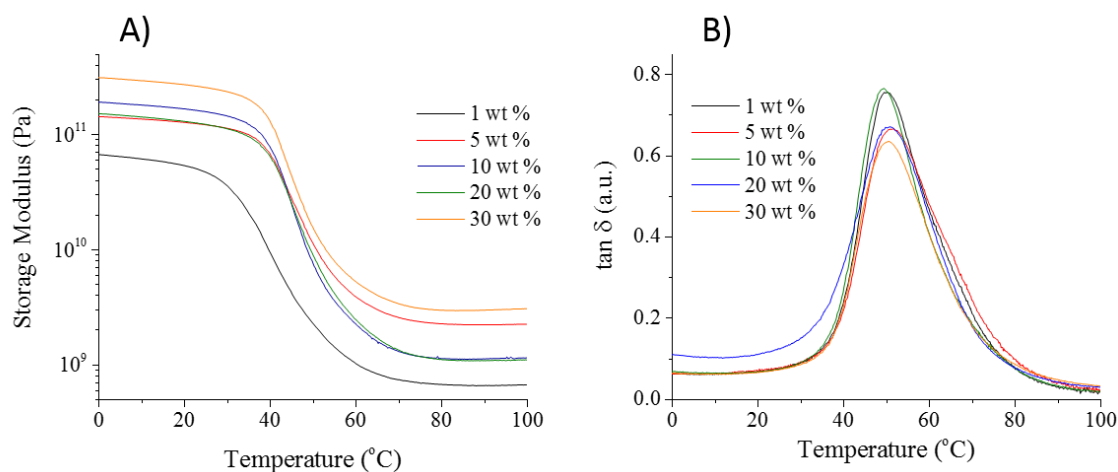


Figure 9: Curves of A) Storage modulus and B) tan δ versus temperature for composites with different MCF contents.

Weight-loss curves of the composites revealed a similar thermal behaviour compared to the unfilled materials, where an initial weight loss event is associate with the loss of low molecular weight compounds (uncured hardener) and a second at higher temperatures related to the thermal decomposition of the cross-links. On the other hand, composites presented residues after the main decomposition events, which was directly proportional to the content of MCF used as reinforcing agent and not observed for previous formulations. This observation is a result of the higher thermal stability of the reinforcing fibres, which does not present any degradation event in this temperature range. Onset temperatures of the main degradation stage and other details regarding the thermal stability of these materials are presented in Table 4 (in comparison to unreinforced formulation with 10 wt% of EPVO) and demonstrated to be comparable to those previously reported. Therefore, the addition of this fibres does not lead to significant changes in the thermal stability of the composite in comparison to the original polymers.

## 4. Conclusion

Thermoset polymers and composites were successfully prepared from virgin, waste and purified vegetable oil samples (rapeseed/palm) blended with commercial epoxy resin based on DGEBA cured

with <span style="color:red">amine-based</span> hardener. These materials characterise the first successful use of such material in this field. Although waste oil-based resins showed poorer tensile properties than the analogous materials from neat and purified oil and produced materials notably more ductile, the use of purified oil-based resins proved to cause no significant sacrifice in mechanical properties in comparison to neat oil when used up to 10 wt %, whilst addition of levels above 15 wt % made the plasticizer character due to proportionally fewer and less reactive oxirane rings as observed by DMA. The addition of recycled carbon fibres permitted achieve and further improve the initial properties of the commercial resin from the addition of 5 wt % of recycled carbon fibres onwards. The best tensile properties were achieved when 30 wt % of fibres were used.  In conclusion, this work demonstrates the potential valorisation of WVO through its use as an alternative source of triglycerides for traditional oleochemistry and opens space for further developments in this area of waste oil-based materials.

## 5. Acknowledgments

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**Figure Captions**

Figure 1: ^{1}H NMR signals affected by the purification procedure: a) the region of aldehydic compounds, B) and C) regions associated mono- and diglycerides.

Figure 2: Schematic representation of the epoxidation methodologies explored in this study

Figure 3: ^{1}H NMR spectra of waste vegetable oil before and after epoxidation (Methodology B) and assignment of the principal signals.

Figure 4: Stress/strain curves of samples with different EPVO content.

<span style="color:red">Figure 5: A) Young`s Moduli, B) elongation at break and C) tensile strength of specimens with different EVO content and different origins.</span>

Figure 6: Curves of A) Storage modulus and B) tan $\delta$ versus temperature for samples with different EPVO oil content.

Figure 7: Thermograms of EPVO-based resins from 25 °C to 600 °C, heating rate of 10 °C min$^{-1}$, under inert atmosphere, and their respective first derivative curve

<span style="color:red">Figure 8: A) Young`s Moduli, B) elongation at break and C) tensile strength of of composites EPVO and different MCF contents in comparison to DGEBA analogous</span>

Figure 9: Curves of A) Storage modulus and B) tan $\delta$ versus temperature for composites with different MCF contents.

Table **Error! Main Document Only.**: Conversion, number of oxirane rings per unit and selectivity of epoxidations with different oil under three methodologies

| Methodology A | | | |
|---|---|---|---|
| No conversion observed. | | | |
| **Methodology B** | | | |
| **Oil sample** | **Conversion (%)** | **Oxirane per Unit** | **Selectivity (%)** |
| Neat | 93 | 2.66 | 93 |
| Waste | 89 | 1.70 | 74 |
| Purified | 93 | 1.82 | 79 |
| **Methodology C** | | | |
| **Sample** | **Conversion (%)** | **Oxirane per Unit** | **Selectivity (%)** |
| Neat | 86 | 2.46 | 85 |
| Waste | 74 | 1.68 | 73 |
| Purified | 90 | 2.03 | 89 |

Table **Error! Main Document Only.**: Maximum curing temperature and enthalpy of curing of samples with different epoxidized oil content.

| EPVO content | Max. Curing Temperature (ºC) | Enthalpy of curing (J g$^{-1}$) |
|---|---|---|
| **0 wt %** | 97.2 | 338.4 |
| **5 wt %** | 88.3 | 250.1 |
| **10 wt %** | 95.2 | 250.0 |
| **15 wt %** | 96.6 | 257.8 |
| **20 wt %** | 96.2 | 249.5 |
| **30 wt %** | 92.4 | 170.2 |

Table **Error! Main Document Only.**: Weight-loss events (onset) and temperature of maximum degradation of samples produced from different epoxidised oils.

| EPVO | 1st Weight-loss event (Onset, °C) | 2nd Weight-loss event (Onset,°C) | $T_{max}$ (°C) |
|---|---|---|---|
| 0 wt % | 153.4 | 345.6 | 369.0 |
| 5 wt % | 159.8 | 344.2 | 360.5 |
| 10 wt % | 156.0 | 342.7 | 360.7 |
| 15 wt % | 129.6 | 345.7 | 367.7 |
| 20 wt % | 125.4 | 334.2 | 363.6 |
| 30 wt % | 112.2 | 328.6 | 355.6 |
| ENVO | 1st Weight-loss event (Onset, °C) | 2nd Weight-loss event (Onset, °C) | $T_{max}$ (°C) |
| 5 wt % | 161.8 | 348.2 | 368.3 |
| 10 wt % | 154.8 | 344.0 | 368.0 |
| 15 wt % | 136.7 | 339.1 | 366.3 |
| 20 wt % | 138.4 | 335.2 | 360.7 |
| 30 wt % | 123.6 | 334.4 | 357.7 |
| EWVO | 1st Weight-loss event (Onset, °C) | 2nd Weight-loss event (Onset, °C) | $T_{max}$ (°C) |
| 5 wt % | 161.2 | 346.0 | 373.0 |
| 10 wt % | 160.3 | 342.4 | 369.1 |
| 15 wt % | 132.4 | 341.6 | 368.3 |
| 20 wt % | 129.1 | 336.5 | 360.3 |
| 30 wt % | 119.1 | 331.6 | 364.3 |

Table **Error! Main Document Only.**: Weight-loss events (onset) and temperature of maximum degradation of composites produced with different milled carbon fibre contents.

| MCF Content | 1st Weight-loss event (Onset, °C) | 2nd Weight-loss event (Onset, °C) | $T_{max}$ (°C) |
|---|---|---|---|
| 0 wt % | 153.4 | 345.6 | 369.0 |
| 5 wt % | 135.4 | 342.9 | 366.1 |
| 10 wt % | 134.6 | 339.9 | 368.9 |
| 15 wt % | 133.1 | 339.5 | 365.6 |
| 20 wt % | 138.4 | 340.2 | 364.0 |
| 30 wt % | 134.2 | 341.6 | 360.8 |