



Synthesis and characterisation of bio-based polyester materials from vegetable oil and short to long chain dicarboxylic acids

Maëlle Gobin, Patrick Louergue, Jean-Luc Audic, Loïc Lemiègre

► To cite this version:

Maëlle Gobin, Patrick Louergue, Jean-Luc Audic, Loïc Lemiègre. Synthesis and characterisation of bio-based polyester materials from vegetable oil and short to long chain dicarboxylic acids. *Industrial Crops and Products*, 2015, 70, pp.213-220. 10.1016/j.indcrop.2015.03.041 . hal-01134645

HAL Id: hal-01134645

<https://univ-rennes.hal.science/hal-01134645>

Submitted on 11 Mar 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis and characterisation of bio-based polyester materials from vegetable oil and short to long chain dicarboxylic acids.

Maëlle Gobin,^{a,b} Patrick Loulergue,^{a,b} Jean-Luc Audic,^{*a,b} and Loïc Lemiègre^{*a,b}

a) Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.

b) Université Européenne de Bretagne, France.

* Corresponding author. Tel. : +33 223238160 ; Fax. +33 223238199

E-mail adress: jean-luc.audic@univ-rennes1.fr

Abstract

Polyester-type polymers were efficiently prepared from broccoli seed oil and several carboxylic diacids. The polyesters were prepared through a simple two-step process including oxidation of the insaturations to oxiranes followed by ring opening with dicarboxylic acids under basic conditions. Eight polymer materials derived from different fatty diacids (from 5C to 16C) and an aromatic diacid were prepared and characterised. Rubber-type crosslinked biobased materials exhibited low T_g values comprised between -5 and +5°C depending on the diacid type and length. These materials could find applications as they are or as plasticizer when blended with other polymers.

Keywords: Bio-based polyesters; epoxidation; epoxidized vegetable oil; broccoli seed oil

1. Introduction

The production of bio-based material is an increasing field of research that aims to replace non-renewable sourced polymers. (Belgacem and Gandini, 2008; Biermann et al., 2011; Chernykh et al., 2013; Meier, 2014; Meier et al., 2007; Montero de Espinosa

and Meier, 2011; Mutlu and Meier, 2010; Stempfle et al., 2014; Xia et al., 2013) Vegetable oils are remarkable renewable resources particularly abundant and cheap. Among them soybean oil is the subject of numerous research topics dealing with applications in polymer material. Indeed, soybean oil finds applications as lubricant, plasticizer or as other types of additives for polymer materials.(Altuna et al., 2011; Chernykh et al., 2013; Montero de Espinosa et al., 2014) Few examples describe also the use of vegetable oil for the preparation of polymer material through direct polymerisation of modified oils.(Maisonneuve et al., 2013; Stemmelen et al., 2011; Tan and Chow, 2010; Winkler and Meier, 2014; Yang et al., 2014) Usually, strategies developed so far for polymerisation of soybean or linseed oils involved multistep triglyceride modification ended by the key polymerisation step.(Biermann et al., 2011; Ma et al., 2013; Stempfle et al., 2014) The most promising strategies involve shorter processes mainly based on anhydride-curing(España et al., 2012; Espinoza-Perez et al., 2011; Ručigaj et al., 2014; Samper et al., 2012) or acid-curing(Shogren et al., 2004; Shogren, 1999) of epoxidised vegetable oil. The present research work focuses on this field with three main goals: 1) Finding new non-food applications for vegetable oils, 2) Developing a polymerisation process leading to potentially biodegradable(Shogren et al., 2004; Shogren, 1999; Yang et al., 2014) polyester-type materials compatible with the use of curing agents of various structures and 3) Determine the influence of the structure of the curing agent used in the polymerisation process. Our choice towards broccoli seed oil (BO) showed up several advantages. This oil is a by-product produced by an extraction process of the food complement industry.(Audic et al., 2014) Its production is actually about 2 tons per year but it could rapidly increase up to 20 tons per year in a near future. The broccoli seed oil is useless for human food industries considering its high erucic acid content (39%). Thus, there is no ethical issue to use such broccoli oil in non-food applications. Broccoli

seed oil is also particularly rich in diunsaturated fatty chains such as linoleic and linolenic acid (22%); in addition it contains an average of 3.9 double bonds per triglycerides as determined by NMR in a previous paper. (Audic et al., 2014)

The polymerisation process described hereafter involves a two-step procedure: a classical oxidation of the double bonds to epoxides and crosslinking by epoxide-opening with dicarboxylic diacids in basic media. Diacids were preferred to anhydrides because of their high availability at low cost and in various molecular structures. Indeed several carboxylic diacids were evaluated, 7 fatty diacids (C5, C6, C8, C10, C12, C14, C16) and 1 aromatic diacid (*o*-phenylene diacetic acid). The efficiency of the chemical reaction involved in the polyester synthesis, i. e. the ring opening reaction of oxirane with carboxylic acid was confirmed by NMR and ATR-FTIR analyses. Corresponding polymer materials were characterised by DMA (Dynamic Mechanical Analysis) demonstrating the potential of these polyester materials and determining the influence of the nature of the diacid (length, structure).

2. Material and methods.

2.1. Synthesis.

All reagents and solvents were used directly from the supplier without further purification unless noted. Nuclear magnetic resonance spectra were recorded at 400 MHz (^1H) and 100 MHz (^{13}C). For CDCl_3 solutions, the chemical shifts (δ) are reported as parts per million (ppm) referenced to the appropriate residual solvent peak. Coupling constants are reported in Hertz (Hz). Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogen atoms, attribution). Abbreviations are as follows: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *dd* (doublet of doublet), *dt* (doublet of triplet), *m* (multiplet), *bs* (broad singlet). The NMR peak assignments were determined from 2D NMR experiments such as COSY,

HSQC, HMBC. Mass spectra were performed on a MS-ESI spectrometer and are reported as m/z . Masses are reported for the molecular ion $[M+Na]^+$.

2.1.1. Epoxidized Broccoli seed oil.

BO (300 g, 0.32 mol, 1 equiv.), toluene (1.4 L) and formic acid (24 mL, 0.64 mol, 2 equiv.) were mixed into a well-stirred reactor. Hydrogen peroxide (35% wt in water) (143 mL, 1.91 mol, 6 equiv.) was added dropwise to the reaction mixture at 50°C. The reaction mixture was kept at the same temperature and monitored by MS-ESI. After 25h, the aqueous phase was extracted twice with toluene and the combined organic phases were dried ($MgSO_4$). The solvent was then evaporated under reduced pressure affording the EBO (319 g, 99%). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm) 0.79-1.01 (m, 9H, CH_3), 1.18-1.77 (m, 86H, CH_2), 2.22-2.27 (m, 6H, $CH_2-C=O$), 2.82-3.15 (m, 7.8H (3.9 epoxides per/molecule), epoxides), 4.07 (dd, $J = 5.9, 11.9$ Hz, 2H, CH_2-O), 4.22 (dd, $J = 4.4, 11.9$ Hz, CH_2-O), 5.17-5.22 (m, 1H, $CH-O$); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm) 14.0 (CH_3), 22.6 (CH_2), 24.8 (CH_2), 26.6 (CH_2), 27.9 (CH_2), 28.9-29.7 (CH_2), 31.9 (CH_2), 34.0 ($CH_2-C=O$), 54.1 (epoxides), 56.7-57.2 (epoxides), 62.1 (CH_2-O), 68.9 ($CH-O$), 172.8-173.3 ($C=O$); MS-ESI m/z $[M+Na]^+$: 927.8, 941.8, 955.8, 969.8, 983.8, 997.8, 1011.8, 125.8, 1039.8, 1053.8, 1067.9, 1081.9, 1095.8.

2.1.2. Reaction of EBO with benzoic acid.

EBO (1.0 g, 1.0 mmol, 1 equiv.) was dissolved in toluene (7 mL). Benzoic acid (244 mg, 2.0 mmol, 2 equiv.) and MeONa (5.4 mg, 0.1 mmol, 0.1 equiv.) were added and the reaction mixture was heated to 110°C. After 96h, AcOEt (10 mL) was added and the reaction mixture was washed with NaOH 1M (2x10 mL) and HCl 1M (10 mL). The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The product was obtained as a yellow oil (1.2 g) with a benzoic acid incorporation of 1.35 per molecule. 1H NMR ($CDCl_3$, 400 MHz), δ (ppm), 0.77-0.85 (m,

9H); 0.97-1.74 (*m*, 95H); 2.22-2.28 (*m*, 6H); 2.83-3.13 (*m*, 3.16H); 3.33-3.50 (*m*, 0.42H); 3.53-3.64 (*m*, 1.11H); 3.73-4.02 (*m*, 0.49H); 4.06 (*dd*, *J*=5.9Hz, *J*=11.6Hz, 2H); 4.21 (*dd*, *J*=4.4Hz, *J*=11.6Hz, 2H); 5.02 (*m*, 1.15H); 5.17 (*p*, *J*=5.2Hz, 1H); 5.40-5.49 (*m*, 0.36H); 7.38 (*t*, *J*=7.2Hz, 3.2H); 7.50 (*t*, *J*=7.2Hz, 1.6H); 7.98 (*d*, *J*=7.6Hz, 3.2H); ¹³C NMR (CDCl₃, 100 MHz), δ (ppm) 14.2, 21.0, 22.5-22.7, 24.8, 25.3, 25.5, 26.6, 27.8, 29.0-29.7, 30.7, 31.8, 33.7, 34.0, 34.1, 54.2, 54.3, 57.2, 60.4, 62.1, 68.9, 72.7, 128.4, 129.7, 130.0, 133.0, 165.9, 166.4, 172.8, 173.3; MS-ESI *m/z* [M+Na]⁺: 927.8, 941.8, 955.8, 969.8, 983.8, 997.8, 1011.8, 1025.8, 1039.8, 1049.8, 1053.8, 1063.8, 1067.9, 1077.8, 1081.8, 1091.8, 1095.8, 1105.8, 1119.8, 1133.8, 1147.8, 1161.8, 1171.8, 1175.8, 1185.8, 1189.8, 1199.8, 1203.8, 1213.8, 1217.8, 1227.8, 1241.8, 1255.8, 1283.8, 1297.8, 1311.8, 1325.8, 1339.8.

2.1.3. General Procedure for the reaction of EBO with diacid.

EBO (3.0 g, 3.0 mmol, 1 equiv.), diacid (6.0 mmol, 2 equiv.) and MeONa (16 mg, 0.3 mmol, 0.1 equiv.) were homogenised at 120°C or at the melting temperature of the diacid. The reaction mixture was poured into an aluminium mould. The aluminium mould was then kept at the same temperature into an oven for 16h. The sample was then characterised by ATR-FTIR and DMA.

2.2. Characterisation of polymer materials

2.2.1. ATR-FTIR.

For IR spectroscopy a Perkin-Elmer Spectrum 100 system infrared spectrometer was used in attenuated total reflectance (ATR) mode using a DTGS detector (4 cm⁻¹ resolution) with the spectral range of 650–4000 cm⁻¹. In these measurements 15 scans were applied and the data were collected and analysed using the Spectrum ES 5.0 software. The sample is placed onto the surface of a diamond prism and the infrared radiation is collected after total reflection from the diamond–sample interface.

2.2.2. DMA.

The viscoelastic properties of the cured films were measured with a DMA instrument (Q800, TA Instruments). Rectangular specimens, 18 mm in length, 13 mm in width and 2 mm in thickness, were prepared. The measurements were taken in single cantilever mode at a frequency of 1 Hz and at deformation amplitude of 20 μm . The temperature ranged from -100 to 100°C at scanning rate of 3°C.min⁻¹. The storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) of the cured films were measured as a function of the temperature.

3. Results and discussion.

3.1. Epoxidized broccoli seed oil (EBO)

The epoxidation of the broccoli seed oil (BO) has been described by our research group in a previous paper.(Audic et al., 2014)It follows a classical procedure involving the *in situ* formation of performic acid from formic acid and hydrogen peroxide that carried out the epoxidation of the 3.9 double bonds of the triglyceride in toluene (Scheme 1). We further optimised the oxidation process reducing the equivalencies of hydrogen peroxide(6 equiv./BO) and catalytic formic acid (2 equiv./BO). The reaction mixture is kept at 50°C for 24h to reach a complete epoxidation as demonstrated by MS and NMR monitoring.

3.2. Model reaction with a monoacid

The so-formed epoxidised broccoli seed oil (EBO) was then ready to react with carboxylic acid functions through an epoxide-opening mechanism. This reaction was first evaluated with a monoacid model for establishing the best reaction conditions in terms of reactivity and reduction of side reactions. The EBO was put in reaction with benzoic acid in the presence of a catalyst at 100°C (Scheme 2). A bronsted acid (*p*-toluene sulfonic acid, PTSA), a lewis acid (ZnCl_2) and a base (MeONa) were evaluated

and the results are gathered in table 1. NMR analysis permitted to follow both the formation of the new ester bonds and the consumption of the epoxides.

When using 4 equivalents of benzoic acid, the bronsted acid gave in 4h (Entry 1) the best conversion in ester derivative (0.40) compared to the lewis acid (Entry 2, 0.30) and the MeONa (Entry 3, 0.20). Concerning the selectivity of the reaction, the sum of ester functions formed and of the remaining epoxide should correspond to the original number of epoxides (3.9) if the desired ester linkage formation is the sole reaction. Otherwise all extra-consumed epoxides result from side reactions. This criterion in mind, the ZnCl_2 is considered as the worst catalyst and MeONa as the best one promoting almost no side reaction. Increasing the reaction time to 24h (Entry 4, 5, 6) confirmed the tendency of PTSA to perform side reactions instead of the formation of ester functions both in the presence of 2 or 4 equivalents of benzoic acid. Finally MeONa was found to favour the formation of ester linkages instead of other side reactions. The best results were obtained with MeONa. The use of only 0.1 equiv. of catalyst in the presence of 2 equiv. of benzoic acid provided in 24h an average of ester functions of 1.35 (maximum of 2) and 2.58 remaining epoxides, corresponding to a conversion of 68%. It is noteworthy that the catalytic amount of MeONa did not lead to methanolysis of the triglyceride as observed on the ^1H NMR spectra (fig. 1). The acid-base reaction between MeONa and the benzoic acid is in fact faster than the alcoholysis.

Side reactions were noticed when using acidic catalysts. EBO dimers and trimers were observed on SEC chromatograms (data not shown). Their formation was correlated to the formation of ether linkages between triglycerides as determined by ^1H NMR experiments. Other research groups dealing with other epoxidized vegetable oils have already described such oligomerisation side reactions. (Shogren, 1999) Note that this acid promoted etherification is also observed in the absence of carboxylic acid.

Compared to these previous works, the reaction conditions described herein the presence of catalytic MeONa provide an advantageous esterification process without side reaction.

3.3. Crosslinking with glutaric acid as model dicarboxylic acid

The best reaction conditions obtained with benzoic acid were adapted to the crosslinking step with dicarboxylic acids (Scheme 3). Bulk type polymerisation was selected removing any solvent, homogenisation of the dicarboxylic acid and the MeONa within the EBO being enough to promote a homogeneous crosslinking of the triglycerides.

As a starting polymerisation experiment glutaric acid and EBO were engaged. Impacts of the reaction temperature (Table 2, Entries 1-6) and the diacid/EBO ratio (Table 2, Entries 7-12) after 4 or 16h of heating were evaluated. Reaction mixtures incorporating an EBO/glutaric acid molar ratio 1:2 (i.e. COOH/epoxide ratio 1:1) were placed at 60, 80, 100, 120, 140, 160 °C in the presence of 0.1 equiv. of MeONa. After 4h, each sample presented different appearance ranging from colourless liquid to brown hard materials. This study at variable temperature led to the following conclusions: the reaction needs to be performed at temperature over 80°C and a suitable polymerisation in 4h is obtained at 120°C, leading to a yellowish translucent polymer. It is noteworthy that this temperature permitted to fully melt the glutaric acid (Mp = 98°C) facilitating its homogenisation within the EBO. Obviously, the EBO/glutaric acid ratio has also a profound impact on the final appearance of the polymers. At that stage the reaction time was increased to 16h to assure as far as possible a complete polymerisation. Too small quantities (0.25, 0.5 equiv., entries 7-8) of glutaric acid did not provide sufficient crosslinking leading to liquid or partly gel-type materials. One equivalent of diacid (entry 9) provided poor crosslinking and offered a brittle polymer

material. Excess of diacid (4 or 6 equiv., entries 11, 12) promoted unsatisfactory crosslinking, the reaction led to a sticky polymer material (4 equiv.) and to a sticky paste (6 equiv.). The excess of carboxylic acid functions limited the crosslinking process to oligomers, keeping most of the acid function untouched. Two equivalents of glutaric acid were finally the best EBO/diacid ratio affording a translucent yellowish polymer (Entry 10).

At a molecular level, ^1H NMR analysis were carried out for samples obtained with 0.5 equiv. of glutaric acid (Table 2, entry 8) the other sample (1, 2, 4, 6 equiv., entries 9-12) being insoluble in any common solvent tried (CHCl_3 , THF, toluene...). The NMR data confirmed both the formation of new ester linkages and subsequent alcohol functions (new signals at 4.9 ppm and 3.5 ppm). It also demonstrated that the integrity of the triglyceride structure is preserved. Quantitatively with 0.5 equiv. of diacid (1 COOH for 3.9 epoxides) we observed the formation of 0.74 (maximum of 1) new ester linkages and 2.6 remaining epoxides. The other reacted epoxides correspond to side reactions identified by NMR to the formation of ether linkages (ring opening polymerisation of the epoxide). After 16h of heating this side reaction is limited to only 0.56. Not observed for the reaction carried out in solution (scheme 2) the formation of ether linkages is present in bulk conditions. However, these reactions still have a lower rate compared to the preferred polyester formation.

The results of the crosslinking step performed with 0.25 to 6 equivalents of glutaric acid (Entry 7-12) were also analysed by ATR-FTIR spectroscopy. The stacked spectra are shown in fig.2. Globally these spectra confirmed the results discussed above. In more details two regions are interesting to discuss 1) the signals related to the epoxide functions around 820 cm^{-1} and 2) the signals related to the carbonyl groups between 1680 and 1750 cm^{-1} . Within the epoxide region, the poorly polymerised

material (0.25 equiv.) demonstrated the presence of residual epoxide functions, the spectra being very similar to the original epoxidized oil. Increasing the number of equivalent of diacid, the epoxide band disappears progressively until total disappearance in the presence of 4 or 6 equivalents of diacid. Within the carbonyl region (i.e. 1700 cm^{-1}), several bands are visible corresponding either to acid or ester functions. Again this region is very similar to the EBO spectra for the material prepared with 0.25 equivalent of diacid. This band corresponds mainly to the ester function of the triglyceride itself. Excess of diacid (4/6 equiv.) led to the appearance of a band at lower wave numbers corresponding to residual carboxylic acid groups. The polymer material obtained with 2 equiv. of glutaric acid presents two ester bands distinguished by different intensities, which originate from the triglyceride and from the new ester functions formed during the crosslinking process. Thus these ATR-FTIR analyses confirmed the degree of polymerisation obtained as a function of the quantity of diacid involved in the reaction. It also confirmed that our polymers correspond mainly to polyester-type materials.

3.4. Crosslinking with different dicarboxylic acids

The best conditions determined for glutaric acid (2 equiv., 120°C , 0.1 equiv of MeONa) were then applied to longer carboxylic diacids (C5, C6, C8, C10, C12, C14, C16) and to o-phenylene diacetic acid (Scheme 3). The temperature of homogenisation was adjusted for each sample as a function of the melting point of each diacid and all polymerisation were carried out at 120°C for 16h (Table 3). Whatever the diacid used the polymerisation led to a yellowish translucent material (Fig.3) except for the aromatic derivative, which led to a brown translucent material.

All polyester materials were then characterised by DMA. Fig.4 shows representative temperature dependence of the storage modulus (E') and loss factor ($\tan \delta$) obtained

from the dynamic mechanical analyses (DMA, at a frequency of 1Hz) of networks prepared in this work (EBO/glutaric acid polyester shown). The $\tan \delta$ curve shows two distinct peaks for all polyesters. The lower temperature peak, located at about -75°C , can only be seen at a lower scale. It is associated with the secondary β relaxation, which was already described in epoxy resins cured with anhydride. (Boquillon and Fringant, 2000) This particular secondary relaxation corresponds to the first drop of the storage modulus (fig.4) and can be more easily associated to the low temperature peak observed on fig.5 representing the temperature dependence of loss modulus (E'') of EBO/glutaric acid polyester. This secondary β relaxation can be associated to the motion of the diester segments created between two crosslinks. (Gerbase et al., 2002)

The second peak of $\tan \delta$ obtained at higher temperature, between -5 and 5°C (Fig.4), corresponds to the second and biggest decrease of the storage modulus and to a significant second peak of loss modulus just below 0°C . This major transition is correlated to the α relaxation and associated to the glass transition temperature (T_g) of the polymer. The α transition temperature is below 0°C (except for aromatic derivative), indicating that polymers are in a rubbery state at room temperature. All data obtained by DMA for all polyesters materials are gathered in Table 4. α and β relaxation temperatures were recorded for each polyester sample from both $\tan \delta$ peaks and loss modulus peaks.

It can be first noticed that increasing diacid length from five to eight carbons first caused a decrease in the α relaxation temperature: determined from $\tan \delta$ peak, this temperature dropped from -1.4 to -4.4°C . From loss modulus data, this temperature also noticeably dropped from -5.7 to -11.4°C . The decrease of the α transition temperature, which corresponds to the glass transition temperature of the polymer could be ascribed to an increase in chain mobility and free volume in the polymer as the diacid length

increased. Nevertheless, when the diacid length further increased from eight carbons to sixteen carbons, the α relaxation temperature gradually increased from -4.4°C to $+4.4^{\circ}\text{C}$ ($\tan \delta$) or from -11.4°C to -2.6°C (loss modulus). It is well known that the crosslinks length influences glass transition temperature. In the present study, for small diacids with less than 8 carbons, the free volume of the material increased as the crosslinks length increased and the glass transition temperature decreased correspondingly (fig.6). For diacids with more than 8 carbons, the further increase in diacid length caused an increase in glass transition temperature. This could be ascribed to the longer methylene sequences in the diacids, leading to enhanced cristallinity and enhanced London dispersion interactions, resulting in stronger restriction in mobility.(Stempfle et al., 2014)This phenomenon is less clearly observed on the β relaxation temperature, but a minimum was also recorded for suberic (C8) based polyester at -73°C ($\tan \delta$ peak) and -77°C (loss modulus peak). When the polyester is synthetized from *o*-phenylene diacetic acid, its α and β transitions temperature, $+16.2$ and -66°C respectively (from $\tan \delta$) are significantly higher than those observed for previous linear diacids. This could be correlated to the presence of aromatic crosslinks organising themselves into more rigid segments.

4. Conclusion

This research work demonstrates that the polymerisation of vegetable oil can be achieved following a two-step process from an extracted oil and aliphatic diacids. The epoxidation/ring opening sequence was first optimised with benzoic acid and then the best conditions (basic media) were applied to several diacids leading to the crosslinking of the triglycerides. It provides an access to original polyester materials not acquirable with other polymerisation strategies (anhydride curing for instance). The conversion of the useless broccoli seed oil to polymer material constitutes therefore a

valuable use of such non-food triglycerides. All polyesters synthesised here were in rubbery state at room temperature because of their relatively low glass transition temperature and they present interesting mechanical properties for numerous applications. It was thus demonstrated that glass transition temperatures (T_g) and also, to a lesser extent, secondary (β) relaxations in the cured polyesters were closely related to the nature and the length of the diacid used in the crosslinking reaction.

Such new kind of green polymers could find numerous applications in the manufacture of environmentally friendly soft and flexible materials. For example, they can be blended with some other polymers in order to decrease their T_g through “permanent” plasticization. On the basis of epoxide ring opening reaction described in this paper, it will be possible to prepare new cured polymers involving other bi-functional (or more) crosslinking agents. Some new additives could also be prepared from epoxidised broccoli oil functionalization. Also it must be noticed that all the chemical modifications and polymerisation processes described in this paper can be applied to other type of oil.

Acknowledgements

The authors acknowledge the financial support of the Region Bretagne and Sojasun Technologies. The authors thank Estelle Guyonvarch for the substantial experimental work done on this project.

References.

Altuna, F.I., Espósito, L.H., Ruseckaite, R.A., Stefani, P.M., 2011. Thermal and mechanical properties of anhydride-cured epoxy resins with different contents of biobased epoxidized soybean oil. *J. Appl. Polym. Sci.* 120, 789-798.

- 323 Audic, J.-L., Lemiègre, L., Corre, Y.-M., 2014. Thermal and mechanical properties of a
324 polyhydroxyalkanoate plasticized with biobased epoxidized broccoli oil. *J. Appl.*
325 *Polym. Sci.* 131, 10.1002/app.39983.
- 326 Belgacem, M.N., Gandini, A., 2008. *Monomers, Polymers and Composites from*
327 *Renewable Resources*. Elsevier Limited, Amsterdam.
- 328 Biermann, U., Bornscheuer, U., Meier, M.A.R., Metzger, J.O., Schäfer, H.J., 2011. Oils and
329 Fats as Renewable Raw Materials in Chemistry. *Angew. Chem. Int. Ed.* 50, 3854-
330 3871.
- 331 Boquillon, N., Fringant, C., 2000. Polymer networks derived from curing of epoxidized
332 lineseed oil: influence of different catalysts and anhydride hardeners. *Polymer* 41,
333 8603-8613.
- 334 Chernykh, A., Alam, S., Jayasooriya, A., Bahr, J., Chisholm, B.J., 2013. Living carbocationic
335 polymerization of a vinyl ether monomer derived from soybean oil, 2-
336 (vinylxy)ethyl soyate. *Green Chem.* 15, 1834-1838.
- 337 España, J.M., Sánchez-Nacher, L., Boronat, T., Fombuena, V., Balart, R., 2012. Properties of
338 Biobased Epoxy Resins from Epoxidized Soybean Oil (ESBO) Cured with Maleic
339 Anhydride (MA). *J Amer Oil Chem Soc* 89, 2067-2075.
- 340 Espinoza-Perez, J.D., Nerenz, B.A., Haagenson, D.M., Chen, Z., Ulven, C.A., Wiesenborn,
341 D.P., 2011. Comparison of curing agents for epoxidized vegetable oils applied to
342 composites. *Polymer Composites* 32, 1806-1816.
- 343 Gerbase, A.E., Petzhold, C.L., Costa, A.P., 2002. Dynamic Mechanical and Thermal
344 Behavior of Epoxy Resins Based on Soybean Oil. *J. Am. Oil Chem. Soc.* 79, 797-802.
- 345 Ma, Q., Liu, X., Zhang, R., Zhu, J., Jiang, Y., 2013. Synthesis and properties of full bio-based
346 thermosetting resins from rosin acid and soybean oil: the role of rosin acid
347 derivatives. *Green Chem.* 15, 1300-1310.

- 348 Maisonneuve, L., Lebarbe, T., Grau, E., Cramail, H., 2013. Structure-properties
349 relationship of fatty acid-based thermoplastics as synthetic polymer mimics.
350 Polymer Chemistry 4, 5472-5517.
- 351 Meier, M.A.R., 2014. Sustainable polymers: reduced environmental impact, renewable
352 raw materials and catalysis. Green Chem. 16, 1672-1672.
- 353 Meier, M.A.R., Metzger, J.O., Schubert, U.S., 2007. Plant oil renewable resources as green
354 alternatives in polymer science. Chem. Soc. Rev. 36, 1788-1802.
- 355 Montero de Espinosa, L., Gevers, A., Woldt, B., Gra, Meier, M.A.R., 2014. Sulfur-containing
356 fatty acid-based plasticizers via thiol-ene addition and oxidation: synthesis and
357 evaluation in PVC formulations. Green Chem. 16, 1883-1896.
- 358 Montero de Espinosa, L., Meier, M.A.R., 2011. Plant oils: The perfect renewable resource
359 for polymer science?! Eur. Polym. J. 47, 837-852.
- 360 Mutlu, H., Meier, M.A.R., 2010. Castor oil as a renewable resource for the chemical
361 industry. Eur. J. Lipid Sci. Technol. 112, 10-30.
- 362 Ručigaj, A., Alič, B., Krajnc, M., Šebenik, U., 2014. Investigation of cure kinetics in a
363 system with reactant evaporation: Epoxidized soybean oil and maleic anhydride
364 case study. Eur. Polym. J. 52, 105-116.
- 365 Samper, M.D., Fombuena, V., Boronat, T., García-Sanoguera, D., Balart, R., 2012. Thermal
366 and Mechanical Characterization of Epoxy Resins (ELO and ESO) Cured with
367 Anhydrides. J Amer Oil Chem Soc 89, 1521-1528.
- 368 Shogren, R., Petrovic, Z., Liu, Z., Erhan, S., 2004. Biodegradation Behavior of Some
369 Vegetable Oil-Based Polymers. J. Polym. Environ. 12, 173-178.
- 370 Shogren, R.L., 1999. Preparation and characterization of a biodegradable mulch: Paper
371 coated with polymerized vegetable oils. J. Appl. Polym. Sci. 73, 2159-2167.

- 372 Stemmelen, M., Pessel, F., Lapinte, V., Caillol, S., Habas, J.P., Robin, J.J., 2011. A fully
373 biobased epoxy resin from vegetable oils: From the synthesis of the precursors by
374 thiol-ene reaction to the study of the final material. *Journal of Polymer Science Part*
375 *A: Polymer Chemistry* 49, 2434-2444.
- 376 Stempfle, F., Ritter, B.S., Mulhaupt, R., Mecking, S., 2014. Long-chain aliphatic polyesters
377 from plant oils for injection molding, film extrusion and electrospinning. *Green*
378 *Chem.* 16, 2008-2014.
- 379 Tan, S.G., Chow, W.S., 2010. Biobased Epoxidized Vegetable Oils and Its Greener Epoxy
380 Blends: A Review. *Polym.-Plast. Technol. Eng.* 49, 1581-1590.
- 381 Winkler, M., Meier, M.A.R., 2014. Highly efficient oxyfunctionalization of unsaturated
382 fatty acid esters: an attractive route for the synthesis of polyamides from renewable
383 resources. *Green Chem.* 16, 1784-1788.
- 384 Xia, Y., Quirino, R.L., Larock, R.C., 2013. Bio-based Thermosetting Polymers from
385 Vegetable Oils. *J. Renew. Mater.* 1, 3-27.
- 386 Yang, D., Peng, X., Zhong, L., Cao, X., Chen, W., Zhang, X., Liu, S., Sun, R., 2014. "Green"
387 films from renewable resources: Properties of epoxidized soybean oil plasticized
388 ethyl cellulose films. *Carbohydr. Polym.* 103, 198-206.