Monitoring the structure-reactivity relationship in epoxidized perilla and safflower oil thermosetting resins†

Thi-Nguyen Tran, a Chiara Di Mauro, a Alain Graillot b and Alice MijaIOD b

For the first time, the effect of reactant structure, stoichiometry and heating rate on the reactivity of epoxidized perilla oil (EPLO) and epoxidized safflower oil (ESFO) with dicarboxylic acids (DCAs) was studied using in situ FT-IR. The epoxy content in the monomer structure was found to affect the copolymerization system’s reactivity, with epoxidized linseed oil (ELO) considered as a reference. In this study we discuss also the influence of the DCA structure on the copolymerization reactivity. Two aromatic diacids, dithiodibenzoic acid (DTBA) and diphenic acid (DPA), were studied and compared in the copolymerization of the 3 EVOs, in the presence of imidazole (IM) initiator. The kinetics of these reactions were followed by in situ FT-IR. The corresponding activation energies were calculated via different kinetic models. These data highlight the higher reactivity of the EPLO monomer and the DTBA hardener.

Introduction

Significant emphasis on serious environmental pollution, restriction of petroleum oil resources, greenhouse gas (GHG) emission, and waste accumulation prompt many scientists to focus on the sustainable development of the chemical industry.1–4 Vegetable oils (VOs) as raw materials are considered to be some of the most promising bioresources because of their availability, advantageous costs, and especially their wide variety of chemical transformations.2,5–10 One common strategy to obtain polymeric materials from VOs is the polymerization of the C=C double bonds on their backbone. Another approach is based on their functionalization. For example VOAs can be functionalized with epoxy groups in a sustainable way. These methods involve the action of hydrogen peroxide and acetic or formic acid, generating the corresponding epoxidized vegetable oils (EVOs), nontoxic products with higher chemical reactivity compared to VOAs. The presence of reactive functional groups together with the possibility of producing them on a large scale make EVOs extremely attractive as green monomers for the bio-based thermosetting resins market.11–14,15 In general, EVOs are mainly composed of triglyceride molecules, which are constituted of three fatty acids bound by a glycerol center through ester linkages.16,17 Although their (macro)molecular structures are similar, different epoxidized vegetable oils have different reactivity from each other. This is related to the chain length, and the number and positions of epoxy groups. The curing process of EVOs has been investigated in numerous studies,1,2,8,18–22 however, to the best of our knowledge, no one has performed a comparison of the structure-reactivity relationship of different EVOs.

The choice of an appropriate curing agent is very important to achieve the designed thermomechanical properties of the cured epoxy resins.23–25 Among several classes of curing agent such as amines, anhydrides, thiols, polyols, etc., carboxylic acids are specifically selected in this study due to their relatively low price, the widespread availability of the raw materials and the good flexibility and weatherability properties of the resulting materials.26 Recently, a new generation of polymer networks has been developed, called “vitrimers”, in which reversible/dynamic chemistries are introduced. These materials offer a possible solution for reprocessing or recycling thermoset materials, thus reducing the impact on the environment and improving the materials’ end of life as well as being a circular economy. The most common dynamic or reversible chemistries used in the creation of vitrimer materials are carboxylate transesterifications,27–29 the transalkylation of triazolium salts,30 olefin metathesis,31 disulfide exchange,32,33 etc.

In many reported studies, materials reprocessing usually takes place with the help of an external stimulus such as UV irradiation34,35 or heating at high temperature,16 or in the pres-
ence of a catalyst.\textsuperscript{27,37} Distinguished from other materials, sulfur-containing moieties (S–S) offer unique opportunities in which exchange can be activated at moderate temperature without any catalyst or initiator.\textsuperscript{32,38–40} Inspired by the strategy of importing exchange bonds from the hardener structure, we used disulfide-containing acids as crosslinkers to design bio-based thermosets with dual dynamic exchange: through (i) carboxylate transesterification, and (ii) disulfide metathesis.

As the properties of polymers depend strongly on their structures, in the case of epoxy thermosets they depend on the structure of both the epoxy monomer and the curing agent. For example, in the case of EVO-based thermosets,\textsuperscript{41–44} a low mechanical strength could result from systems with high content of flexible backbones and/or low crosslink density. In contrast, the use of appropriate curing agents could reinforce significantly the strength and modulus of EVO-based thermosets. Therefore, the most important key parameter in materials development is the structure-reactivity-properties relationship. It can help to predict and therefore to design the properties and performances of the final products formed through a given manufacturing process. In this context, this work reports for the first time the comparison of 3 EVO cross-linking reactions with aromatic diacids, and the structure-reactivity relationships and kinetics were studied through FT-IR.

To monitor the cure kinetics of thermosetting resin, Fourier Transform Infrared (FT-IR) spectroscopy and Differential Scanning Calorimetry (DSC) are two common techniques. DSC experiments can be performed to obtain kinetic parameters, which make it possible to simulate the curing. However, DSC only gives information about the overall process and not about the elemental reactions that occur during curing. Therefore, FT-IR spectroscopy is specifically selected as an interesting alternative to monitor the curing kinetics. Indeed, mid-infrared spectroscopy is the most suitable technique for following epoxy–hardener crosslinking reactions. It should be noted that many FT-IR spectral frequencies change in a significant way during this reaction, correlated to the nature and number of reacting groups in the crosslinking mixture. These changes can be monitored. Both qualitative and quantitative information can be obtained using this technique which provides a direct measurement of the evolution in concentration over time and temperature of any chemical group involved in the reaction. Furthermore, this method allows us to process the data and therefore to compute the kinetic parameters of the investigated reaction, i.e. conversion degree ($\alpha$), reaction rate ($d\alpha/dt$), and activation energy ($E_a$).

Results and discussion

Previously, we demonstrated that the use of imidazole as initiator provides efficient epoxy/acid crosslinking, generating thermosets with tunable thermomechanical properties. In the present study, we selected 3 different EVO monomers with three levels of epoxide content varying from 3.7 to 8.0 equivalents per mole. The curing of these 3 EVOs with 2 dicarboxylic acids (DCAs), namely 2,2′-dithiodibenzoic acid (DTBA) and diphenic acid (DPA), was investigated by \textit{in situ} FT-IR analysis. The effect of epoxy monomer and crosslinker on the curing kinetics is studied in this work.

General characteristics of the FT-IR spectra

\textbf{Epoxidized vegetable oils (EVOs).} From the FT-IR spectra illustrated in Fig. 1 we can firstly observe that the 3 EVOs, \textit{i.e.} EPLO with 8 eq. epoxide per mole, ELO with 5.5 eq. epoxide per mole and ESFO with 3.7 eq. epoxide per mol, have very similar absorptions, since their structures are also very similar. The principal FT-IR absorption peaks are: $\mathrm{\delta(CH_2)}$ asymmetric stretching at 2947 cm$^{-1}$; $\mathrm{\delta(CH_2)}$ symmetric stretching at 2854 cm$^{-1}$; and $\mathrm{C=O}$ stretching of the ester triglycerides at 1740 cm$^{-1}$. The asymmetric O–C–O stretching band of the ester groups appears at 1150 cm$^{-1}$ and the C–O ether stretching bands for the $\alpha$-positions of the ester groups are located at 1095 and 1115 cm$^{-1}$.\textsuperscript{4,46,47} Two specific absorptions of the oxirane ring are observed in the range between 4000 cm$^{-1}$ and 400 cm$^{-1}$. The first one, at about 823–847 cm$^{-1}$, is attributed to the C–O deformation of the oxirane group.\textsuperscript{36,48} The second band is located at ~3050 cm$^{-1}$ and is attributed to the C–H stretching of the methylene group of the epoxy ring. Due to its low intensity and very close vicinity to the strong O–H absorption, it is preferable to use the first band, located at about 823 cm$^{-1}$, to quantify the conversion degree of epoxy groups.

\textbf{Dicarboxylic acid hardeners.} The common peak assignments of the two selected DCA hardeners are summarized in Table S1.\textsuperscript{†} Similar to all carboxylic acids, the O–H stretching vibration band is very broad in the region of 3300–2300 cm$^{-1}$ with a maximum at 2813 cm$^{-1}$ (Fig. 2). This band is overlapped with the stretching vibration region of the aromatic C–H groups. We observe also other common characteristic peaks including: $\mathrm{C=O}$ stretching at about 1674 cm$^{-1}$; C–O stretching at 1320–1000 cm$^{-1}$ and O–H bending at $\sim$1450 cm$^{-1}$ and $\sim$900 cm$^{-1}$.\textsuperscript{12,49,50} The characteristic peaks in the aromatic region are observed at $\sim$1590 and $\sim$740 cm$^{-1}$ for the two ortho-substituted benzene rings.

\textbf{EPLO/DTBA/IM system}

A FT-IR comparison of the starting materials with the reactive EPLO/DTBA/IM mixture and the thermoset is presented in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{FT-IR spectra of the three EVO monomers, namely EPLO, ELO, and ESFO.}
\end{figure}
remark that the two strong absorption peaks of IM at 934 and as one of the bands of the EPLO oxirane ring. However, we can and in-plane ring deformation, are located in the same region of the IM absorption bands. Two bands for IM at about

\[ |5090 \]

Fig. 4. Evolution of FT-IR spectra during heating from 25 °C to 180 °C at 10 °C min\(^{-1}\), comparing the 3 mixtures: (1): ELO/DTBA/IM; (2) DTBA/IM; (3): ELO/IM.

The first method uses the peak at 1586 cm\(^{-1}\) as the reference band. This band corresponds to C=\(\equiv\)C stretching in the aromatic ring. The second method uses the peak at about 736 cm\(^{-1}\) as a reference, which is attributed to C–H bending of the ortho-substituted aromatic ring. The corresponding results are presented in Fig. 5A. The results obtained by both methods allowed confirmation of the reference peak choice and of the conversion calculation.

For the ELO/IM mixture, a slight decrease in the band intensity of the epoxy rings at 847 and 823 cm\(^{-1}\) is observed. Moreover, we can remark that this band remains present in the case of ELO/IM mixture while the temperature increases up to 180 °C. This indicates that some epoxy rings are still present, whereas some of them have already reacted with IM to form an epoxide/imidazole intermediary complex as shown in Scheme 1. During the heating of the DTBA/IM mixture we observe widening of the absorption bands at 1674 cm\(^{-1}\), 1463–1391 cm\(^{-1}\) and \(\sim 895\) cm\(^{-1}\). This suggests the formation of carboxylate groups (COO\(^{-}\)) due to the basicity of IM.

Concerning the EVO/DTBA/IM reactive mixture, the FT-IR spectra recorded during the curing reveal the gradual diminution of the peaks at 1678 and 895 cm\(^{-1}\), corresponding to the C=\(\equiv\)O stretching and O–H bending of DTBA, together with the twin oxirane C–O bands of EVO at 823 and 847 cm\(^{-1}\). At the same time, a progressive increase in the intensity of the peak at 3600 cm\(^{-1}\), characteristic of the hydroxyl groups [–OH], and the appearance of a new ester peak located at about 1705 cm\(^{-1}\) are observed. The epoxy, carboxyl and ester groups absorb in

Fig. 3. Table S2† summarizes the corresponding assignments of the IM absorption bands. Two bands for IM at about 823–847 cm\(^{-1}\), corresponding to N–H out-of-plane bending and in-plane ring deformation, are located in the same region as one of the bands of the EPLO oxirane ring. However, we can remark that the two strong absorption peaks of IM at 934 and \(\sim 618\) cm\(^{-1}\) together with the peak at 1540 cm\(^{-1}\) are missing in the FT-IR spectrum of the reactive mixture, at the initial time. Considering that only 1 wt% of IM is included in the reactive mixture, the lack of peaks indicates that the IM signals are negligible compared to those of EPLO and DTBA.

To evaluate the interactions of each component during the imidazole catalyzed epoxy–acid crosslinking, in situ FT-IR measurements were performed on the mixtures ELO/DTBA/IM, EPLO/IM and DTBA/IM using the same heating rate from 25 °C to 180 °C. The corresponding spectra are displayed in Fig. 4.

Evaluation of the peak area for the epoxy groups at about 823–847 cm\(^{-1}\) allows us to follow the progress of the ring opening reaction. The extent of the crosslinking reaction was quantified by the peak area for the epoxy group absorption at about 823 cm\(^{-1}\) in reference to the internal standard. Two methods were applied to calculate the epoxy conversion, using eqn (5) as described in the Experimental section of the ESL†

Fig. 2 FT-IR spectra of the two hardeners: 2,2’-dithiodibenzoic acid (DTBA) and diphenic acid (DPA).

Fig. 3 FT-IR spectra of the starting materials, namely EPLO, DTBA, and IM, in comparison with the reactive mixture at the initial time and the corresponding cured resin: (A) whole spectrum from 4000 to 500 cm\(^{-1}\); (B) close-up of the region from 1800 to 1500 cm\(^{-1}\); (C) close-up from 950 to 600 cm\(^{-1}\).

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Influence of heating rate on ELO/DTBA/IM curing

FT-IR spectroscopy was employed to monitor the structural changes during the curing of the ELO/DTBAsystem (R = 1) at different heating rates, namely 5, 10, 15, and 20 °C min⁻¹. The corresponding results are presented in Fig. 6.

Fig. 6A indicates clearly that the heating rate had a great influence on the conversion degree. As expected, the curing reaction accelerates on increasing the heating rate. The relationship between reaction rate (da/dt) and curing time is depicted in Fig. 6B. The reaction rate increases at higher heating rates during the entire conversion. Obviously, the fastest reaction rate was obtained with a heating rate of 20 °C min⁻¹, at which a strong reaction acceleration is observed. The maximum rate of reaction is achieved during the first minutes and then the rate decreases very fast. Moreover, this high heating rate is not preferred for polymer production since we cannot control the network formation as the rate of reaction is so high.

For the other three heating rates, 5, 10, and 15 °C min⁻¹, we can observe in Fig. 6 that the curing kinetics can be divided into two stages. The conversion rate rises slowly and gradually reaches a maximum value, then decreases progressively at the end. This suggests that the heating rate has a big impact on the curing kinetics and thus strongly affects the reaction mechanism in the first step of the non-isothermal curing process.

Influence of EVO monomer reactivity

The effect of the EVO’s chemical structure on the EVO/DTBA/IM curing was studied using stoichiometric amounts of epoxy/acid compounds (R = 1). This ratio was revealed to be the most favorable for EVO/DCA curing, avoiding secondary reactions (etherification, Fisher esterification). Under this condition (R = 1), the copolymerization reaction is more selective, leading to the formation of hydroxyl ester products.

The plots of degree of conversion (α) as a function of the curing temperature and of time are exhibited in Fig. 7. The initial slope of the conversion curve is sharpest for EPLO followed by the ELO and ESFO systems. However, the slope gradually decreases after a certain temperature (T ~ 110 °C). This result is explained in the literature for epoxy/anhydride systems by the change from a kinetically-controlled stage to a diffusion-controlled stage.⁵¹,⁵²,⁵³ The authors interpret this result by an autocatalyzed-initiated mechanism for the curing process with the initial stage consisting of the formation of a “reactive” species (i.e. zwitterion-carboxylate). In the second stage, as the curing reaction proceeds, the reaction rate increases significantly to a maximum value when the concen-
be related to the slightly lower molecular weight, and therefore  
ELO/DTBA/IM, even though the epoxy content of ELO is higher  
beginning of the reaction, (5092

Kinetic model fit  

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<th>Kinetic model fit</th>
<th>EPLO</th>
<th>ELO</th>
<th>ESFO</th>
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<tr>
<td></td>
<td>DTBA</td>
<td>DPA</td>
<td>DTBA</td>
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<tr>
<td>First order</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$\alpha &lt; 0.4$</td>
<td></td>
<td>48</td>
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<tr>
<td>$R^2$</td>
<td>0.9947</td>
<td>0.9988</td>
<td>0.9977</td>
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<tr>
<td>Second order</td>
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<td>$\alpha &lt; 0.4$</td>
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<td>55</td>
<td></td>
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<tr>
<td>$R^2$</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9924</td>
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$R^2$: linear correlation coefficient.
merization in systems outside the stoichiometric ratio. In fact, when the concentration of DCA is higher than that of EVO, there is very little diffusion of reagents, due to the very high viscosity induced by the DCA, and consequently the conversion and reaction rate are lower compared with those of the \( R = 1 \) system.

Influence of the hardener structure

The effect of the chemical structure of the aromatic diacid hardener was studied for \( R = 1 \). A comparison is made here between DTBA and diphenic acid (DPA), an aromatic hardener which doesn’t contain disulfide S–S bonds. Regarding the chemical structures of DPA and DTBA (Chart 1), it is obvious that the presence of sulphur in the \( \beta \) position of the carboxylic group in the DTBA molecule increases the reactivity of its acidic proton toward the epoxy group.\(^{54}\) As expected, higher reactivity of DTBA towards oxirane groups is observed for all EVOs during the first steps (lower temperature). For example, in the case of the EPLO/DTBA/IM system the conversion \( \alpha = 0.5 \) is achieved at a temperature of \(~70^\circ C\) whereas in the case of EPLO/DPA/IM the same conversion is achieved only at around \( 97^\circ C \) (\( \Delta T \sim 27^\circ C \)) (Fig. 10).

In contrast, DPA become more reactive at higher conversions: \(~0.88\) for EPLO/DPA/IM, and \( 0.60 \) and \( 0.38 \) respectively for ELO/DPA/IM and ESFO/DPA/IM. This could be due to the lower melting temperature of DPA (230 °C vs. 290 °C for DTBA)

![Fig. 9](https://example.com/fig9.png)

Fig. 9 Plots of conversion (\( \alpha \)) as a function of temperature (A), and plots of reaction rate \( d\alpha/dt \) as a function of time (B) and conversion (\( \alpha \)) (C).
and therefore the lower viscosity of the mixtures. In the first steps, the epoxy–acid reaction is controlled by the reactivity of the comonomers. Thereafter, the crosslinking becomes diffusion-controlled.

Obviously, the epoxy/acid ratio affects both the reaction order and the $E_a$ of the crosslinking reaction. The amount of catalyst or initiator affects only the apparent $E_a$. For the same epoxy/acid ratio, the reaction order ($n$) should remain unaffected. Consequently, we applied $n$ = 1 (first order) and $n$ = 2 (second order) to estimate the $E_a$ for the 3 EVOs reacting with the two aromatic dicarboxylic acids at $R$ = 1 in order to compare the reactivity of these systems. The same methods are applied for all crosslinking systems and the fitted results are given in Table 1.

For both applied methods, the same trend in activation energy was obtained: higher $E_a$ values for ESFO among the 3 EVOs and for DTBA among the two hardeners. The $E_a$ is higher during the first stages of the curing process, i.e. for $\alpha < 0.4$ and then it diminishes when $\alpha$ increases. This can be explained by a combination of physical and chemical factors that act during the curing process. It is supposed that at the beginning of the curing, the reaction mechanism is dominated by the chemical reactivity and in the later stages it is controlled by physical diffusion. The $E_a$ values are in the range of 40–100 kJ mol$^{-1}$ and decrease from 74 to 48 kJ mol$^{-1}$ when the epoxy content increases from 3.7 eq. per mole to 8.0 eq. per mole in the case of the EVO/DTBA/IM systems. The same relationship between $E_a$ and epoxy content is observed for the systems with the DPA hardener. The fitted $E_a$ values for EPLO, ELO, and ESFO are 43, 53, and 66 kJ mol$^{-1}$, respectively, assuming that the reaction mechanism is first order.

**Kinetic analysis**

Generally, epoxy/hardener crosslinking is characterized by a quite complex mechanism. The competing reactions involved are related to different kinetic equations, but the rate of reaction can be formulated from three different variables, namely temperature $T$, extent of conversion $\alpha$, and pressure $P$, as presented in eqn (1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P)$$  \hspace{1cm} (1)

In most curing processes, the effect of pressure is usually not considered because no gas takes part in the reactions, so the rate of reaction depends on only two variables ($T$,$\alpha$)

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$  \hspace{1cm} (2)

where $k(T)$ is the temperature-dependent reaction rate constant and is defined by the Arrhenius equation:

$$k(T) = A \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (3)

where $E_a$ represents the activation energy, $R$ is the universal gas constant equal to 8.3145 J K$^{-1}$ and $A$ is the pre-exponential factor. The function $f(\alpha)$ is the model representing the reaction mechanism governing the curing process, dependent on the curing degree. It can be simulated by various reaction models. In general, $f(\alpha)$ for epoxy curing is usually hypothesized to follow an $n^{th}$ order reaction model.

After some derivation, the following equation is obtained:

$$\ln \left( \frac{G(\alpha)}{T^2} \right) = \ln(A) - \frac{E_a}{RT}$$  \hspace{1cm} (4)

By plotting $\ln \left( \frac{G(\alpha)}{T^2} \right)$ versus $1/T$, a linear dependence is obtained with a slope of $-E_a/R$. Therefore, the activation energy ($E_a$) can be calculated from this slope. The reaction model equations are shown in Table 2. The $f(\alpha)$ model fitting is validated by the best correlation coefficient ($R^2$) for the

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**Chart 1** Chemical structures of epoxidized safflower oil (ESFO), epoxidized linseed oil (ELO) and epoxidized perilla oil (EPLO), the two hardeners dithiodibenzoic acid (DTBA) and diphenic acid (DPA), and the imidazole (IM) initiator used in this study.

**Fig. 10** Conversion ($\alpha$) of EVO/DTBA/IM systems as a function of temperature in comparison with EVO/DPA/IM, obtained by FT-IR analysis: EPLO/DTBA/IM vs. EPLO/DPA/IM (A); ELO/DTBA/IM vs. ELO/DPA/IM (B) and ESFO/DTBA/IM vs. ESFO/DPA/IM (C).
Table 2 Possible expressions for \( f(a) \) and \( G(a) \) for different kinetic models

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<thead>
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<th>Order</th>
<th>Expression</th>
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<tr>
<td>Third</td>
<td>((1 - a)^3)</td>
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<td>(n)th</td>
<td>((1 - a)^4)</td>
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Limiting surface reaction between both phases
One dimension \(\alpha\) Two dimensions \(2(1 - a)^{1/2}\) Three dimensions \(3(1 - a)^{1/3}\)
Diffusion
One-way transport \(1/2a\) Two-way transport \([−\ln(1 - a)]^{-1}\)

The straight line \((\ln(G(a))/T^2 \) versus \(1/T)\) as obtained by empirical methods. In this study, when \(R = 1\), we assume that only epoxy/acid esterifications occur during the curing. First order and second order kinetic analyses were applied to the FT-IR data.

Conclusions
This work explores the influence of EVO epoxy content on the kinetics of EVO/DCA copolymerization. The obtained results reveal that the EVO/DCA reaction depends strongly not only on the degree of epoxidation but also on the type of vegetable oil (i.e. degree of unsaturation).

Moreover, in this work, for the first time the activation energy was calculated via only the simple FT-IR technique. We have successfully demonstrated that a structure–reactivity relationship exists in these systems. Thus, EPLO is revealed as the most reactive monomer as a consequence of its high epoxy content. The obtained results prove that it is possible to predict and modulate the EVO/DCA reaction kinetics in order to design bio-based thermosets with desirable and competitive properties. The influence of diacid chemical structure was also investigated. The presence of dynamic S–S bonding in the \(β\) position of the carboxylic group increases the reactivity of the acidic proton toward the epoxy group, and therefore produces an increase in reactivity.

Experimental section
Materials
Epoxidized linseed oil (ELO, average molecular weight = 980 Da; average functionality = 5.5 epoxides per triglyceride) was supplied by Valtris Specialty Chemicals. Epoxidized perilla oil (EPLO, average molecular weight = 1227 Da; average functionality = 8.0 epoxides per triglyceride) and epoxidized safflower oil (ESFO, average molecular weight = 960 Da; average functionality = 3.7 epoxides per triglyceride) were supplied by Specific Polymers. 2,2′-Dithiodibenzoic acid (DTBA, ≥95%), diphenic acid (DPA, ≥97%), and imidazole (IM, ≥99%) were purchased from Sigma Aldrich. All chemical compounds were used as received without any further purification and are presented in Chart 1.

Fourier-transform infrared spectroscopy (FT-IR)
The crosslinking reaction kinetics was monitored in situ using a Thermo Scientific Nicolet iS50 FT-IR spectrometer with a deuterated \(\alpha\)-alanine doped triglycine sulfate (DLαTGS) detector in attenuated total reflectance (ATR) mode. To prepare the formulations, all components were pre-mixed at room temperature, and then cured in situ during heating from 25 to 180 °C at a selected heating rate (5, 10, 15 or 20 °C min\(^{-1}\)). The FT-IR spectra were recorded each minute during heating. The absorption bands were recorded in the range of 600–4000 cm\(^{-1}\) with 32 scans and a resolution of 2 cm\(^{-1}\). The data were analysed using the OMNIC software. The conversion of functional groups at time \(t\) is denoted by \(a\) and defined by eqn (5).

\[
α = \left(\frac{A_{\text{functional groups}}}{A_{\text{ref}}} \right)_{0} - \left(\frac{A_{\text{functional groups}}}{A_{\text{ref}}} \right)_{\text{ref}} t
\]

The area of the absorbance peaks was calculated and reported for different times \(A_{\text{ref}}\) after the initial time \(A_{\text{ref}}\). The band at about 823 cm\(^{-1}\) corresponds to the oxirane C–O groups and that at about 895 cm\(^{-1}\) corresponds to the carboxylic groups. Two methods of calculation were applied for the epoxy conversion. The first method used the peak at 1386 cm\(^{-1}\) as the reference band, which corresponds to \(δ_{C–C}\) for the aromatic rings. The second method used the peak at about 736 cm\(^{-1}\) as a reference, which is attributed to C–H bending of the ortho-substituted aromatic rings. Each sample was prepared and analysed in triplicate to ensure efficiency, reliability and reproducibility.

Sample preparation
The EVO/DCA copolymerizations were carried out in the presence of 1% (w/w) of imidazole as initiator. The ratio \(R\) is defined as the ratio of epoxy groups to carboxylic acid groups according to the literature.\(^{55}\) The initiator was first dissolved in EVO at around 80 °C and the solution was mixed together. Then, at room temperature, the selected DCA was added and the solution was mixed until complete homogenization. The freshly prepared samples were analysed by FT-IR to follow the copolymerization reaction.

Abbreviations

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<tr>
<td>EVO</td>
<td>Epoxidized vegetable oil</td>
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<tr>
<td>ELO</td>
<td>Epoxidized linseed oil</td>
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<tr>
<td>EPLO</td>
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</tr>
<tr>
<td>ESFO</td>
<td>Epoxidized safflower oil</td>
</tr>
<tr>
<td>DCA</td>
<td>Dicarboxylic acid</td>
</tr>
<tr>
<td>DTBA</td>
<td>2,2′-Dithiodibenzoic acid</td>
</tr>
<tr>
<td>DPA</td>
<td>Diphenic acid</td>
</tr>
<tr>
<td>IM</td>
<td>Imidazole</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
</tbody>
</table>
Conflicts of interest

There are no conflicts to declare.

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Notes and references

20 X. Huang, X. Yang, H. Liu, S. Shang, Z. Cai and K. Wu, Bio-based thermosetting epoxy foams from epoxidized soybean oil and rosin with enhanced properties, Ind. Crops Prod., 2019, 139, 111540.
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