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PLANT-BASED RESINS OBTAINED FROM EPOXIDIZED LINSEED OIL USING A MgAl HYDROTALCITE CATALYST

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In the intent of obtaining plant-based resins with various properties, epoxidized linseed oil (ELO) with an average of 6 epoxy groups per molecule has been cured with different amounts of phthalic anhydride (PA). The reactions were performed using a base heterogenous catalyst, MgAl hydrotalcite with Mg/Al molar ratio 3. The obtained materials were characterized through various methods and the results were interpreted, showing that the curing reactions were successful. This work shows that using heterogenous catalysis is a viable way of obtaining cured materials from vegetable oils.

Keywords: epoxidized linseed oil, phthalic anhydride, heterogenous catalysis

1. Introduction

Vegetable oil is an abundant renewable raw material which is considered for replacing petroleum based chemicals used industrially, with the intent of reducing pollution [1-2]. The major component of these materials are triglycerides, which are esters of glycerol with saturated or unsaturated fatty acids. The fatty acid composition of vegetable oils determines their properties, and in consequence, their uses as raw materials [3].

Vegetable oils can be used as such in the food industry and as bio lubricants [4]. One of the most important uses is the production of biodiesel through the transesterification reaction [5]. However, the double bonds present in the alkyl chain of the unsaturated fatty acids open the possibility for obtaining a large variety of compounds using functionalization reactions [6]. An important part of the intermediaries obtained through reactions such as metathesis, hydroformylation or epoxidation can be used as monomers in the polymer industry [7]. The epoxidation reaction is particularly important for the macro industry because it leads to versatile epoxidized vegetable oils that can be cured with a wide variety of compounds (amines [8], acids [9], anhydrides [10]) or that

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can undergo ring opening reactions, leading to interesting end-products and intermediaries.

Anhydrides are some of the most efficient curing agents for epoxidized vegetable oils (EVO) due to their increased reactivity with their internal epoxy groups [2]. The ring opening reaction is complex, with several competing steps taking place at the same time [11]. Curing EVOs with anhydrides leads to thermoset polymers with thermo-mechanical properties heavily influenced by the epoxy content of the vegetable oil, the anhydrides used and the molar ratio between reactants[12]. The curing reaction is catalyzed by Lewis bases, such as tertiary amines or imidazole [13].

In order to achieve a cleaner and more environmentally friendly process, the idea of using heterogenous basic catalysts for epoxy ring opening reactions has been tested. Fogassy et. al [14] have used weak bases, such as hydrotalcites, and stronger bases, the mixed oxides obtained from the calcination of the aforementioned hydrotalcites for opening the ring of epoxidized fatty acid methyl esters with acetic anhydride. The goal of the study consists in the preparation of materials based on epoxidized linseed oil cured with phthalic anhydride (PA) using an affordable base heterogenous catalyst, the MgAl hydrotalcite. This is a layered double hydroxide (LDH), which is a class of materials with the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}{}_{x/n}]\cdot mH_2O$, where $\boldsymbol{M^{2+}}$ and $\boldsymbol{M^{3+}}$ are divalent and trivalent cations in the brucite-type layers, $\boldsymbol{A}$ is the interlayer anion with a $\boldsymbol{n}$ charge balancing the exceeding charge occurring by isomorphic substitution of M^{2+} by M^{3+}, $\boldsymbol{x}$ is the fraction of the trivalent cation and $\boldsymbol{m}$ is the crystallization water [15]. To the best of our knowledge, this catalyst is not previously reported in literature for the curing of epoxidized vegetable oil with PA, this paper presenting the first attempt of using it in such reaction. However, this type of catalyst was often used for a broad range of reactions [16], such as epoxidation [17], isomerization of double bonds [18], reduction of nitro compounds [19], aldol condensation [20], Knoevenagel condensation [21], Michael addition [22] and so on, and it is well characterized [23].

2. Materials and methods

2.1 Materials

The epoxidized linseed oil (ELO) was prepared via the epoxidation of commercial linseed oil (LO) using a method previously reported in literature [24] which employs a Prilezhaev mechanism of reaction (Fig. 1) [25]. Linseed oil (LO) obtained by cold-pressing process was acquired from PTG Deutschland, Flurstedt, Germany. The toluene used as solvent and the phthalic anhydride were purchased from Sigma Aldrich. The PA was purified by dehydration and the toluene was used as such. The MgAl LDH catalyst was used in a previous study and prepared and characterized as such [26].

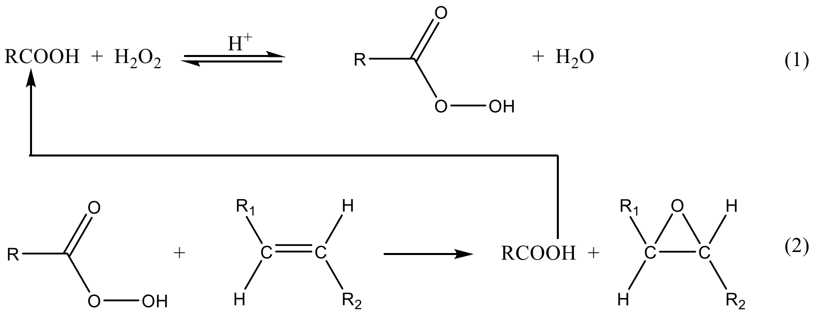

Fig. 1: The mechanism of the Prilezhaev reaction used, with the generation of the peracid in situ (1) and the subsequent epoxidation of the substrate (2)

2.2 Epoxidation of linseed oil

Prior to the reaction, the average unsaturation of the LO was determined, using a ^1H NMR technique which can also estimate the fatty acid composition of vegetable oils [27]. A number of 6 double bonds per triglyceride molecule was determined, as well as the average composition in linolenic acid (50% wt), linoleic acid (15% wt), oleic acid (20% wt) and saturated acids (15% wt).

LO, acetic acid, and 50% (vol.) sulfuric acid are dissolved in toluene solvent. The appropriate volume of H_2O_2 (30% vol.) is then added dropwise at room temperature, stirring constantly. The temperature is raised to 60 °C once all the H_2O_2 has been added, and the reaction mixture is kept under constant stirring for 24 hours. The molar ratio of double bonds to acetic acid to H_2O_2 is 1:2:10, with the double bonds being considered per molecule of triglyceride. The organic and aqueous phases were separated when the reaction was completed. The organic phase was rinsed with distilled water and saturated sodium bicarbonate solution until a neutral pH was achieved, to eliminate traces of acid and hydrogen peroxide. After that, the organic solvent was evaporated under vacuum, yielding a semisolid white product (95% yield) which was subsequently characterized through ^1H NMR.

^1H NMR (δ in ppm, $CDCl_3$ solvent, TMS standard): 0.9 (t, terminal -C**H**$_3$ from all fatty acids except linolenic acid), 1.03-0.95 (m, terminal -C**H**$_3$ from linolenic acid), 1.28-1.20 (m, -C**H**$_2$- from all alkyl chains), 1.57-1.44 (m, -C**H**$_2$-CH$_2$-COO), 1.76-1.67 (m, -C**H**$_2$- between epoxy rings), 2.26 (t, -C**H**$_2$-COO acyl group), 2.91 (m, C**H** marginal protons from the epoxy ring), 3.1 (m, C**H** internal protons of the epoxy ring), 4.1-4.23 (m, -C**H**$_2$-O-CO-, glycerol protons in α positions), 5.2 (m, -C**H**-O-CO-, glycerol proton from β position). The epoxidation was considered quasi-total, based on comparing the ^1H NMR spectra of the LO and ELO. It can be observed that the signals assigned to the chemical shifts of the vinyl protons of the unsaturated oil (δ = 5.2-5.35 ppm) present in the LO spectrum are not found in the ELO spectrum. Instead, the spectrum of the product contains the signals of the protons from the epoxy rings, and the signal integral is consistent with 6 epoxy groups per triglyceride molecule.

2.3 Epoxidized linseed oil curing

ELO and PA in different molar ratios were dissolved in 10 mL of toluene solvent. The MgAl LDH catalyst was added (10% wt), and the mixture was heated to 100 °C and kept under constant magnetic stirring for 24 h. The reaction mixture was then cooled, and the catalyst was filtered. The organic liquid phase was washed with water 4 times for the removal of unreacted phthalic anhydride. The solvent from the organic phase was removed under vacuum. A part of the product was soluble in $CDCl_3$ (deuterated chloroform) and was analyzed by ^1H NMR. The insoluble part was also recovered, which was suspected as being the cured resin, and was analyzed using IR spectroscopy, simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) coupled with mass spectrometer (MS).

2.4 Characterization

^1H NMR was used to study the structures of ELO and the obtained materials. The samples were dissolved in 0.5 mL $CDCl_3$, and the spectra were recorded using a Gemini Varian 300 MHz instrument. The relaxation delay was set to 2 s with 32 scans. The spectra were calibrated using the chloroform signal (7.26 ppm).

The solid materials were characterized by FTIR spectroscopy with a Bruker VERTEX 70 instrument, equipped with a Harrick MVP2 diamond ATR device.

The thermal analyses of the obtained materials were performed using a NETZSCH STA 449C Jupiter simultaneous TGA-DSC system at 10°C · min^{-1}, under He inert gas coupled with an Aeolos 2 mass spectrometer.

3. Results and discussion

The curing reactions were performed with different molar ratios between the ELO epoxy groups and PA. The average epoxy group content per triglyceride molecule was determined by adapting a previously described ^1H NMR method for the characterization of vegetable oils [27]. The molar ratio between reactants was adjusted for obtaining cured materials with different thermo-mechanical properties [12].

The first reaction was performed using a molar ratio between the ELO groups and PA of 1:0.6, with the intent of reacting half of the epoxy groups to obtain a cured material with viscoelastic properties [28]. The reaction product, a viscous liquid, was analyzed using ^{1}H NMR and FT-IR spectroscopy. The ^{1}H NMR spectra of the obtained liquid product (Fig. 2) shows a 50% reduction of the integral of the epoxy group specific signal (2.9-3.1 ppm), having an integral of 6, compared to the signal of the ELO epoxy groups, which has an integral of 12, indicating a 50% conversion. The signals were integrated using the signal of the proton from the β position of the glycerol (5.2 ppm) as internal standard. The presence of aromatic signals specific to PA (~7.8 ppm) confirm that the epoxy rings were opened with PA.

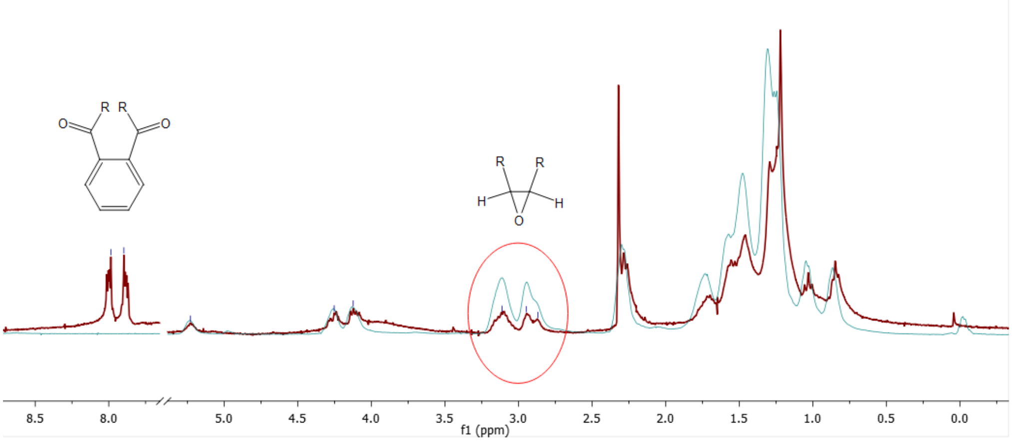

Fig. 2: The superimposed ^{1}H NMR spectra of ELO (green) and the partially epoxy ring-opened liquid product (red)

The IR spectra also show a partial consumption of the epoxy groups, evidenced by the decreased intensity of the epoxy band (830 cm^{-1}) (Fig. 3). The spectrum of the product has additional bands specific to aromatic stretching (3020 and 1594 cm^{-1}) compared to the spectra of ELO, which indicates the presence of the phthalic moieties. Also, the band specific to aliphatic ester stretching, present at 1740 cm^{-1} for ELO, is shifted to 1727 cm^{-1} in the spectra for the liquid product. This could be explained by the formation of new aromatic esters, which typically give absorption bands between 1715-1730 cm^{-1}, confirming the ring-opening and esterification with PA. A molar ratio of 1:0.6 (epoxy groups to PA) leads to a partial conversion of the epoxy groups, with the obtaining of a partially epoxy ring-opened liquid material. In order to highlight the changes made to the structure of the vegetable oil during the curing, the characteristic IR stretches, and their attribution have been presented in Table 1.

Table 1

FT-IR peak assignments for ELO and the cured products

Wavenumber (cm^{-1})	Assignment
830	Epoxy group C-O-C stretching
1225	C-O stretch from esters
1594	Aromatic ring stretching
1727	Aromatic ester stretching
1740	Aliphatic ester stretching
2927, 2857	-CH_2 and -CH aliphatic stretching
3020	Aromatic ring stretching

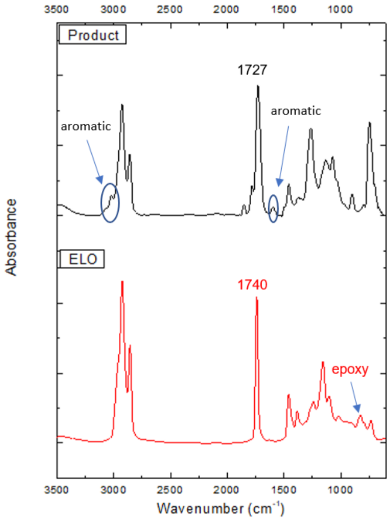

Fig. 3: FT-IR spectra of ELO (red) and the obtained product from the partial ring-opening (black)

Aiming to obtain a rigid resin, the opening of all the epoxy groups was attempted. The molar ratio of 1:1.2 (epoxy groups to PA) was used, with the obtaining of a solid product, suspected as being the cured material, which was designated as R1. The product is not soluble in common deuterated solvents and the NMR analysis couldn`t be performed. The FT-IR analysis showed a large decrease of the epoxy group band at 830 cm^{-1}, which indicates the near total consumption of the epoxy groups. Aromatic stretches which indicate the presence of phthalic moieties have been observed (3020 and 1594 cm^{-1}), along with the 1740 cm^{-1} stretching specific to ester groups. This led to the decision of further increasing the PA excess to a molar ratio of 1:1.5 (epoxy groups to PA). The obtained resin, designated as R2, was also analyzed by FT-IR, which showed the total consumption of the epoxy groups and, as in the case of R1, the ring-opening of the epoxy groups with phthalic anhydride.

With the purpose of confirming the obtaining of cured resins using LDH catalyst, another curing of ELO with PA has been performed, using a well-known method previously reported in literature, which employs 1-methylimidazole as catalyst [29]. The FT-IR spectrum of the obtained solid product, presented below (Fig. 4), is similar to the spectra of the resins previously obtained in this study.

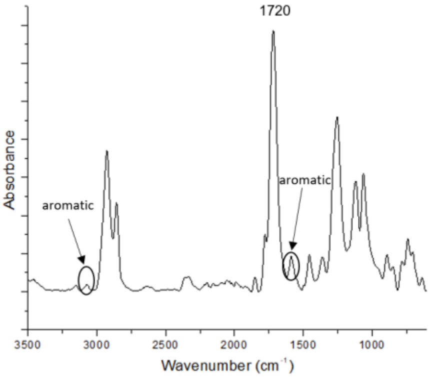

Fig. 4: FT-IR spectrum of the material obtained from the curing of ELO with PA in the presence of 1-methylimidazole

The thermal degradation behavior was studied using the TGA-DSC-MS method. The TGA analysis (Fig. 5) shows that the thermal degradation of the R1 sample starts earlier than that of R2, which suggests that R2 has a higher thermal stability than R1. This is due to the higher curing ratio of the R2 sample, which is consistent with the larger excess of PA used, compared with R1. All the results are confirmed by the previous observations made while interpreting the FT-IR spectra. Also, it can be observed that the thermal degradation is made of 2 steps, which are more evident in the case of R1. This further confirms that R1 is less thermally stable, and thus, has a lower curing ratio than R2.

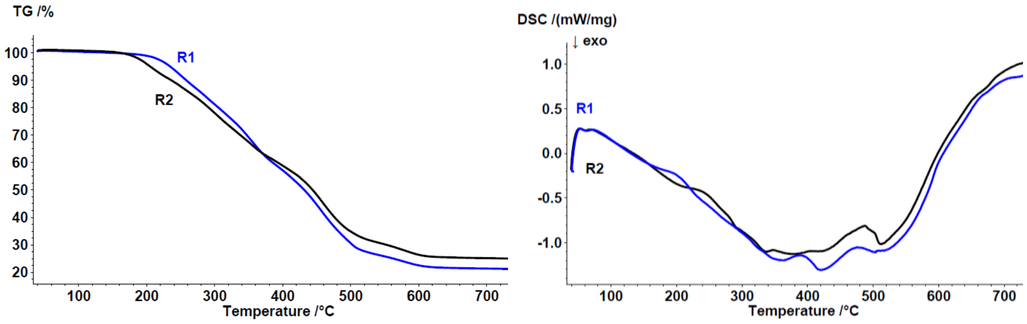

Fig. 5: The TGA and DSC thermograms showing the degradation behavior of the resins at a heating rate of 10°C · min^{-1}, under He inert atmosphere

The MS coupled with TGA-DSC shows the mass distribution of the fragments which leave the molecule during the thermal decomposition (Fig. 6,

Fig. 7). The MS spectra at the maximum degradation speed confirms the presence of fragments specific to H_2O, CO, CO_2, and benzene. This further confirms the presence of resins cured with PA.

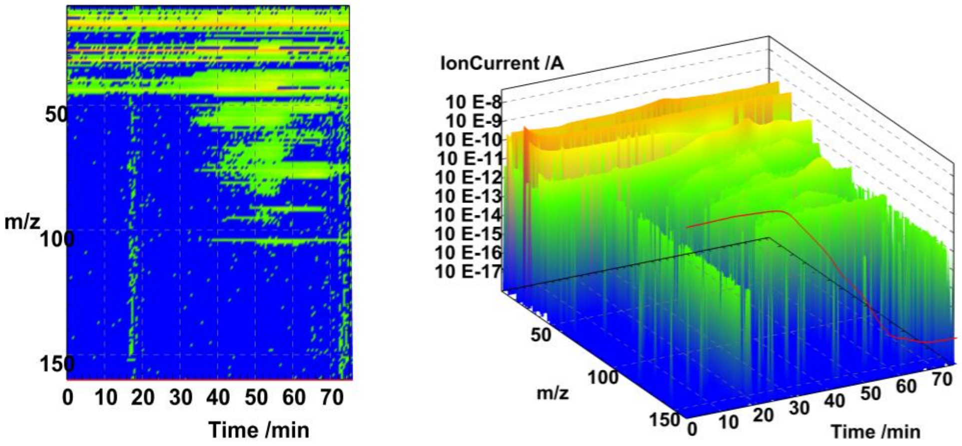

Fig. 6: The 2D (left) and 3D (right) mass spectra of the R1 sample, showing the distribution of the mass fragments during the thermal degradation

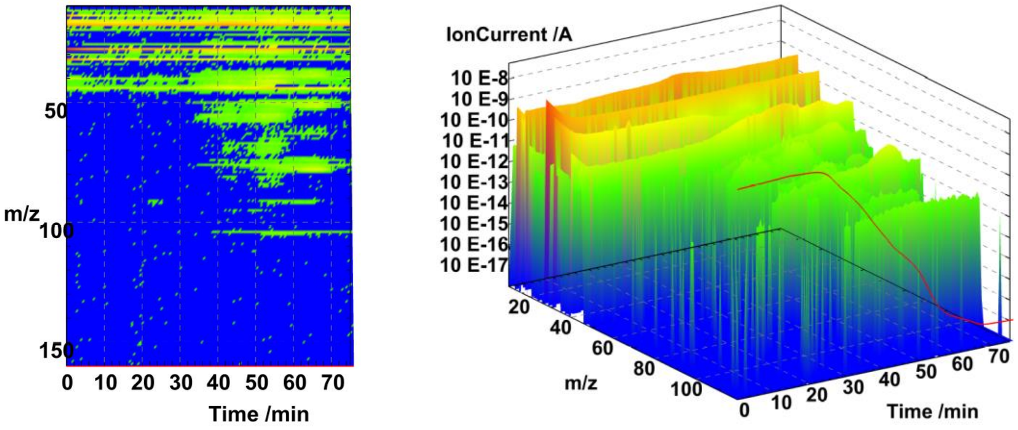

Fig. 7: The 2D (left) and 3D (right) mass spectra of the R2 sample, showing the distribution of the mass fragments during the thermal degradation

4. Conclusions

Plant-based resins with different properties were obtained by reacting epoxidized linseed oil and phthalic anhydride in different molar ratios, in the presence of a solid catalyst with potential for reusability, MgAl LDH. Spectroscopy methods showed the ring-opening of the epoxy groups and the appearance of phthalic moieties in the obtained product. The curing was confirmed by the thermal analysis of the solid products, which shows the thermal degradation behavior of the samples, as well as the fragments leaving the product during this process, the curing ratio being influenced by the PA excess. Using MgAl LDH as catalyst allows curing epoxidized vegetable oil with PA to obtain materials with potential application in the polymer industry, which may be a viable alternative to traditional curing.

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