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Epoxy Methyl Soyate as Bio-Plasticizer: Two Different Preparation Strategies

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Due to the recent rise in production costs of biodiesel and considering the necessity to use environmentally friend production way, bio-plasticizers obtained from vegetable oils were developed. Bio-plasticizer are essentially constituted by epoxidized vegetable oils (EVO) (rich in unsaturated compounds as soybean, sunflower and rapeseed oils).These kind of products have got good plasticizer properties and are easily biodegraded by microbial agents. The main advantages of these additives are their low diffusion coefficients in the polymeric matrix and a very low volatility. In recent years epoxidised fatty acid methyl esters (EME) have been developed, because they are more soluble and confers better flexibility to the plastic even at low temperatures. The main problem associated with these products lies in their content of satured methyl esters. This fraction cannot be epoxydised and has got a very low affinity with the polymeric matrix, so that tends to migrate at the plastic surface giving not desired properties to the final products. The aim of this work is to find the best reaction conditions in terms of epoxide yield, using acetic acid and hydrogen peroxide, and to apply these condition either to 1) a fractionated biodiesel (i.e. without satured esters) or 2) to soybean biodiesel in order to obtain EME and then distillate it to remove the unreacted esters. Both the strategies were studied by experimental batch epoxidation test and vacuum distillation runs. A better bio-plasticer was obtained (epoxide number of about five) using the first strategy, i.e. by a distillation of starting biodiesel, perfomed at 0.5 torr using a two equilibrium stage batch distillation apparatus, followed by the epoxidation reaction.

1. Introduction

1.1 Bio-plasticizer

A plasticizer is a molecule that improves the fluidity and the plasticity of polymeric materials, i.e. plastics, paints and adhesives (Wypych, 2004). In order to achieve this, two different solutions are used, the internal plasticization and the external plasticisation. The first one consists in either modifying the polymer chemical structure or using a co-polymer with different mechanical characteristics to obtain a final macromolecule more flexible. The term external plasticization is used when suitable additives are added into the polymeric matrix. These latter are called plasticizers and generally are liquids which have got poor affinity with the polymeric matrix, thus that do not form a chemical bond with the polymer. The external plasticizer can be divided into two main categories: 1) Primary, which directly determine the mechanical characteristics of a polymer (e.g. in PVC are added up to the 30 %vol) and 2) Secondary, which reduce the polymer rigidity but have got poorer performances compared to the primary plasticizer. Usually they are used in small quantities and mixed with the primary plasticizer in order to increase their effectiveness. The external plasticizers could be classified by considering them chemical structure. Above all the groups, with particular reference to PVC, the phthalate family is one of the most famous. Phthalates are obtained from phthalic acid (or phthalic anhydride) with a primary alcohol, i.e. 2-ethyl-hexanol, and are used as plasticizer in a lot of applications. Recently EU has forbidden the di-octyl phthalate use in plastics used for the production of toys and PVC food packaging. Due to the recent increasing request for new economically sustainable chemical products, bio-plasticizers have been developed. These are epoxidized vegetable oils

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(EVO) (Soo-Jin et al, 2004), and era obtained from renewable resources. Bio-plasticizers possess good plastic properties and are easily bio-degraded. The main drawback of these materials (which have been available on market for some years) is their low solubility in the polymeric matrix, hence they are used mainly as secondary plasticizers (Park et al, 2004). One of the advantages of bio-plasticizers is that they are characterized by a very low diffusion coefficient and a very low volatility. Also the lubricant power of these molecules makes them helpful during the plastic lavoration.

1.2 Epoxy Biodiesel

Epoxidized fatty acid methyl esters (EME) are more soluble in the polymeric matrix than EVO and confer excellent flexibility to the final product also at low temperatures and, therefore, can be used as primary plasticizer. Biodiesel is a mixture of fatty acid methyl esters produced from vegetable oils, exhausted oils or animal fats by transesterification reaction with methanol using a strong base as catalyst (Rios et al, 2012). It can be used as solvent, lubricant, fuel or as a precursor for added value chemicals. Epoxidized biodiesel is used either as bio-plasticizer or as an intermediate for the bio-lubricant synthesis. As it could be imagined only the unsatured molecules contained in biodiesel (mainly methyl oleate) can react to give epoxidised biodiesel. Also the affinity of the unreacted molecules (i.e the satured one) for the polymeric matrix is less and thus these latter tend to migrate at the plastic surface and give problems such as transudation. In this work epoxidized biodiesel was produced from soybean oil biodiesel with the in-situ epoxidation catalyzed by sulphuric acid using hydrogen peroxide and acetic acid as oxygen carrier (Goud et al, 2006) adopting two different strategies: a) by distillating biodiesel in order to remove its satured components (mainly constituted by methyl palmitate and stearate) and then epoxidising the residue and b) by producing epoxy biodiesel using a commercial biodiesel and then eliminating the unreacted molecules (i.e. the satured compounds and the unreacted unsatured molecules) by distillation. Both a) and b) strategies produced an epoxy biodiesel richer in epoxide groups compared to a commercial biodiesel epoxidized. The product obtained using both the strategies were compared in order to choose the best way to produce an epoxidized biodiesel with the highest oxyrane content possible.

2. Experimental

All the reagents for the epoxy biodiesel synthesis and for the analysis were purchased from Sigma-Aldrich without further purifications. Soybean biodiesel was kindly given by Cereal Docks Spa (Italy). The epoxidation reaction was conducted in a 1 L flask under mechanical agitation. The temperature was kept constant using a thermostatic bath. Both biodiesel and acetic acid were directly charged in the reactor while hydrogen peroxide and sulphuric acid were added dropwise in 15 min at 40 °C (Smith et al., 2009). When their addiction was terminated, the temperature was raised at the operative reaction temperature. Every sampling (about 10 mL) was put in a separating funnel and 10 mL of a satured solution of $NaHCO_3$ was added to neutralize all the acid. The mixture then was washed with distilled water until neutral pH. After have let the oil phase to separate, it was collected and dried under vacuum. The same procedure was followed for the reaction mixture at the end of the reaction. The composition of biodiesel was determined by chromatographic analysis (EN 14103, 2011), using a GC-FID Hewlett Packard HP 5890, equipped with a Supelco Omegawax® 320 column (L × I.D. 30 m × 0.32 mm, df 0.25 μm), using He as carrier and a split ratio 1:100. The calibration was made using the standard Supelco GLC-10 FAME mix. Methyl octanoate was used as internal standard and hexane as solvent. The epoxide content in the epoxidised biodiesel samples was expressed as oxyrane oxygen (OO) content, whose unit is oxygen gram per 100 g sample. The oxyrane oxygen content was determined following the AOCS Method Cd 9-57. It consists in a titration of the sample, diluted in acetic acid, using a standardized HBr solution in acetic acid and crystal violet as indicator. The double bond conversion was evaluated from the GC analysis by calculating the iodine number (IN) while the epoxy biodiesel selectivity using the following equation:

$$\text{Selectivity } [\%] = \frac{\mathrm{OO_{exp}}}{\mathrm{OO_{the}}} * 100 \tag{1}$$

where OOexp is the experimental epoxide number at time t while OO_{the} is the epoxide number calculated from the IN at time t. The distillations were carried out either using a simple Claisen distillator for separating the epoxy biodiesel from the unreacted molecules or using a vigreaux (to have a higher number of theoretical trays) for the separation of satured methyl esters from the unsatured methyl esters for the biodiesel. The reboiler temperature was controlled by the use of a thermocouple with a precision of 1 °C and the pressure was monitored using a digital manometer MKS instruments t. 116A. A set of reactions was conducted to find which experimental condition gave the maximum selectivity toward the epoxide compounds. In particular it was studied the influence of the amount of acetic acid and hydrogen peroxide on the final epoxy biodiesel yield. These optimal set of operative parameters were used for epoxidising both the biodiesel and the distilled biodiesel.

3. Results and discussion

3.1 Epoxidation reaction optimization

A set of 12 experimental runs were performed to identify the optimal reaction conditions. In Table 1 both the operative parameters and the experimental results are shown. The aim of this study was the achievement of the maximum epoxide yield, limiting the oxyrane ring opening reaction.

Table 1: Operative parameters for the in-situ epoxidation of biodiesel with hydrogen peroxide

RUN	Temperature [°C]	Mol AA/mol DB	Mol H_2O_2/mol DB	Catalyst amount [%w H_2SO_4]	Conversion t =6 h [%]	Selectivity t = 6 h [%]
A	60	1.0	1.0	0.0	13.3	67.6
B	60	1.0	1.0	1.0	50,2	85,2
C	60	0.5	1.5	1.0	53.2	93.3
D	60	0.5	2.5	1.0	74.8	86.7
E	60	0.25	2.5	1.0	43.5	97.9
F	**60**	**1.0**	**2.5**	**1.0**	**83.5**	**83.8**
G	50	0.25	2.5	1.0	29.3	72.1
H	60	0.25	2.5	2.0	71.5	63.2
I	60	0.5	2.5	2.0	96.3	54.2
L	60	1.0	2.5	2.0	100.0	29.8
M	50	0.10	1.0	1.0	5.4	84.1
N	60	0.50	2.5	2.0	100.0	7.8

The operative parameters of RUN F were chosen to perform the epoxidation of the distilled biodiesel because they give the highest yield above the all tested. With these parameters an EE with an oxyrane oxygen content of 2.61 was obtained. In Figure 1 the experimental results expressed as double bond conversion and oxyrane oxygen are shown.

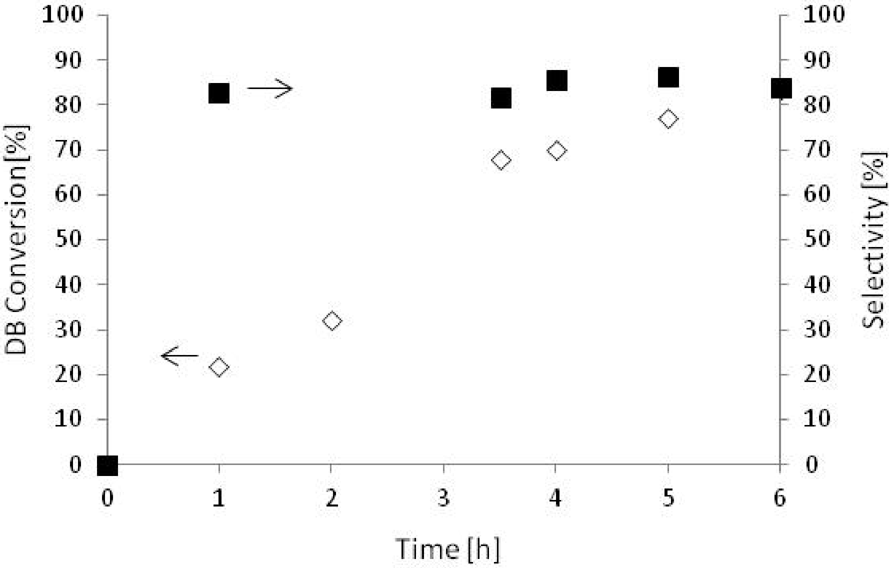

Figure 1: RUN F experimental results, molAA/molDB=1.0, MolH2O2/molDB=2.5, %w H2SO4=1.0

3.2 Bioplasticizer preparation

3.2.1 Strategy *a*: biodiesel distillation, then epoxidation

As previously explained, the distillation of biodiesel was performed using a vigreaux distillation apparatus. After the characterization of the feedstock used (methyl soyate) a distillation curve determination at a head pressure of 0.13 mbar was run to optimize the distillation parameters. The overall pressure drop, experimentally measured with a manometer, was 2.3 mbar. The results are shown in Figure 2, in which 180.55 g of biodiesel with a mass percentage of satured components of 24.0% was distilled.

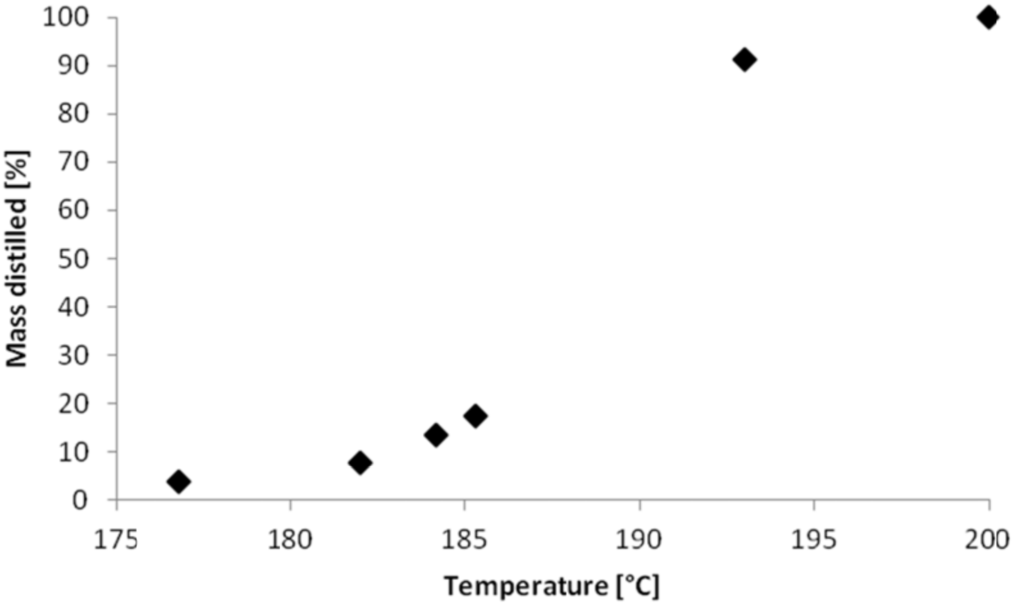

Figure 2: Soybean biodiesel experimental distillation curve, P_{head}=0.13 mbar

Considering the acidic composition of soybean biodiesel, in which in average 25 % by weight are represented by satured molecules (i.e. methyl palmitate and methyl stearate), the obtained results permitted us to work at the properly operative temperatures in order to maximize the unsaturation content in the residue.

A distillation was then carried out setting the boiler temperature at 187°C in order to distillate about the 50 % of the mixture and the biodiesel remained in the reboiler was epoxidized with the experimental parameters previously determined. The results are shown in Table 2:

Table 2: Experimental results for strategy a (biodiesel distillation, then epoxidation)

Time [h]	IN [gI$_2$/100g]	OOthe [gO/100g]	OOe [gO/100g]	DB Conversion [%]	OO Selectivity [%]
0	120.6	0.0	0.0	0.0	0.0
1	93.8	1.6	1.1	22.3	71.9
2	63.4	3.4	2.1	47.9	63.5
3	43.7	4.6	3.0	63.1	65.2
4	25.9	5.6	3.6	78.4	64.6
5	17.1	6.1	3.9	85.5	64.1
6	9.5	6.5	4.2	92.0	64.7

These results show that epoxidising a feedstock with an increased concentration of unsaturation results in a final product with a higher OO content. The value of OO selectivity was found to be lower than the one obtained in RUN F. This experimental results could be interpreted as either a “solvent effect”, in which the satured molecules help to decrease the solubility of the acetic acid in the biodiesel phase thus reducing the ring-opening reaction or in an increasing in the side reactions rate due to the higher number of epoxide ring available in the mixture (the double bonds are concentrated). In order to investigate the results an experimental epoxidation using a distilled biodiesel but adding cyclohexane to compensate the distilled satured compounds was carried out. The choice of the cyclohexane molecule was made because it is poorly soluble in water and it is volatile, so that can be evaporated at the end of the reaction. The experimental results are summarized in Table 3:

Table 3: Experimental results for epoxy biodiesel synthesis using a solvent

Time [h]	IN [gI_2/100g]	OOthe [gO/100g]	OOe [gO/100g]	DB Conversion [%]	OO Selectivity [%]
0	120.60	0.00	0.00	0.00	0.00
1	95.23	1.57	1.05	21.03	66.59
2	60.23	3.67	2.29	50.06	62.50
3	43.64	4.63	3.03	63.81	65.58
4	29.70	5.42	3.63	75.37	67.01
5	19.76	5.98	4.09	83.62	68.39
6	10.93	6.47	4.78	90.93	73.99

As can be observed from the results, the reaction with a solvent gave approximately the same results obtained without using it. For this reason it was concluded that the decrease in epoxide selectivity was due for kinetic reasons as previously explained.

3.2.2 Strategy b: epoxidation, then epoxy biodiesel distillation

As previously described the second strategy consists in the distillation of an epoxy biodiesel sample in order to separate the satured fraction from the unreacted unsatured molecules, which possess a higher volatility compared to the epoxidised compound. The epoxidised biodiesel obtained using the optimized parameters was distilled at 0.1 mbar setting the boiler temperature at 190 °C. The mass charged in the reboiler was 200 g. The distillation was termined when the 30 % of the total mass was distilled, using the reflux due to the vapour condensation on the distillator wall (estimated at 0.1). In Table 4 the results in terms of OO are summarized:

Table 4: experimental results of epoxy biodiesel distillation

Sample	OO [gO/100g]
Epoxy biodiesel	4.25
Epoxy biodiesel, distillatet	2.42
Epoxy biodiesel, reboiler	4.28

As can be observed although in the distillate the OO content decreases (i.e. the unreacted molecules are concentrated in the distillate as expected), in the reboiler the OO content remains constant. This is due to the high residence time needed to distillate the unreacted molecules. Long residence time in the boiler in fact, cause an excessive re-opening of the epoxy ring with a consequent lowering of the OO content of the plasticizer. A mass balance considering the OO of both distillate and the epoxy biodiesel remained in the reboiler permits to calculate the amount of epoxide degradated, which corresponds to the 15 % of the one charged. An indication to the fact that the thermal degradation of the epoxide ring was happened was the changed colour of the mixture: from a transparent solution with a viscosity at 25 °C similar to the one of methyl soyate a yellowish mixture was recovered from the distillator reboiler. This mixture also possessed a viscosity surely higher than the one of the feedstock. A solution to these operative problems relies in using evaporation techniques characterized by short residence time in the apparatus (i.e. thin film evaporation). Both the samples prepared with the two different strategies were compared with two different commercial bioplasticizer derived from methyl soyate, NPPX (an Indian product) and REFLEX100 (by PolyOne Srl), which possess an OO content of 4.96 and 6.38 respectively.

4. Conclusion

Epoxidised biodiesel has been prepared with the in situ epoxidation reaction using hydrogen peroxide, acetic acid as oxygen carrier and sulphuric acid as catalyst. Two different production strategies were compared to obtain a plasticizer with better performances compared with an epoxy biodiesel produced from biodiesel. The epoxy-biodiesel prepared by reacting a biodiesel with a higher iodine value possessed an oxyrane oxygen content comparable with the one of a commercial bio-plasticizer. The distillation of an epoxy biodiesel sample seemed to be a preferable choice to obtain a higher oxyrane oxygen content but the too high temperatures required influenced the re-opening of the epoxide. Short residence time evaporation will be taken into account for the preparation of bioplasticizer with improved performances avoiding the degradation due to the high temperatures.

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