



Lubricants from chemically modified vegetable oils

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ABSTRACT

This work reports laboratory results obtained from the production of polyols with branched ether and ester compounds from epoxidized vegetable oils pertaining to annual, temperate climate crops (soybean, sunflower and high-oleic sunflower oils), focusing on their possible use as components of lubricant base stocks. To this end, two different opening reactions of the epoxide ring were studied. The first caused by the attack with glacial acetic acid (exclusively in a single organic phase) and the second using short-chain aliphatic alcohols, methanol and ethanol, in acid media. Both reactions proceed under mild conditions: low synthesis temperature and short reaction times and with conversions above 99%. Spectroscopic (NMR), thermal (DSC) and rheological techniques were used to characterize the oils, their epoxides and polyols, to assess the impact of the nature of the vegetable oil and the chemical modifications introduced, including long-term storage conditions. Several correlations were employed to predict the viscosity of the vegetable oils with temperature, and good agreement with the experimental data was obtained.

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1. Introduction

New technologies aimed at the development of products from renewable sources have emerged during the last decade, due to increased concerns over the use of petroleum-based products caused by the progressive depletion of the world reserves of fossil fuels, but also owing to concerns on their environmental impact.

In this regard, vegetable oils (VO) constitute a suitable alternative for replacing ‘mineral oils’, as they are wholly biodegradable, non-toxic, and ‘Generally Regarded as Safe’ (GRAS) products (Erhan and Perez, 2002; Erhan and Asadauskas, 2000). Indeed, VOs possess most of the desirable lubricity properties, such as good contact lubrication, high viscosity index (i.e., minimum changes in viscosity with temperature), high flash-point and low volatility. They also have drawbacks, however, that must be overcome, including poor low-temperature properties (such as opacity, precipitation, poor flowability and/or solidification at relatively moderate temperature), their susceptibility to oxidative degradation and their propensity to undergo hydrolysis in acid media. The latter, nevertheless, can be attenuated with relative ease through the use of additives (Hwang and Erhan, 2001; Hwang et al., 2003).

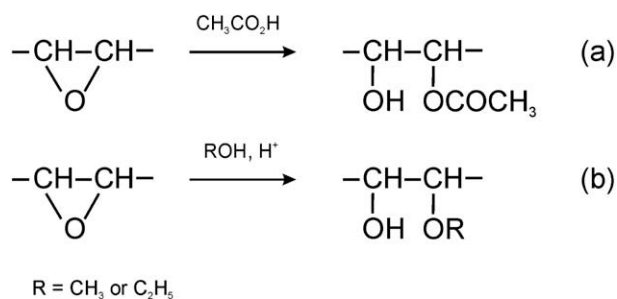
Deliberate modification of the chemical structure of VOs is a sound alternative to allow their direct use as lubricant basestocks. For instance, unsaturated alkene groups of the fatty acid chains in triglyceride molecules can be deliberately altered to give more

complex structures that improve both the low-temperature and oxidative stability properties (Erhan and Perez, 2002; Lathi and Mattiasson, 2006; Hwang and Erhan, 2001; Hwang et al., 2003; Adhvaryu et al., 2005; Sharma et al., 2006, 2008).

Epoxidized vegetable oils are promising intermediates for the utilisation of VO given that the epoxide, or oxirane, group can be easily functionalized. Erhan and co-workers (Erhan and Perez, 2002; Hwang and Erhan, 2001; Hwang et al., 2003; Erhan et al., 2008) recently worked on the production of lubricant base stocks from acid-catalyzed oxirane ring-opening reactions using epoxidized soybean oil, employing several alcohols and later esterifying the resulting hydroxyl group with an acid anhydride. They also synthesized a biolubricant from di-hydroxylated soybean oil, obtained by acid hydrolysis of the epoxide group followed by esterification of said hydroxyl groups (Adhvaryu et al., 2005; Sharma et al., 2006). More recently, they also produced acyl derivatives of soybean oil via the opening of the oxirane ring using acid anhydrides and employing BF_3 etherate as catalyst. These products appear to be promising lubricants (Sharma et al., 2008).

In recent years, there has been an increased interest in the production of biodiesel (BD) as a more benign fuel. BD is usually produced by the transesterification of vegetable oil triglycerides with an aliphatic alcohol (such as, methanol) employing sodium hydroxide as a catalyst. Fatty acid methyl ester (FAME) are obtained as the main product of this reaction. Thus, FAMES have become extensively available and are produced with high purity. This has opened new pathways to the synthesis of oleochemical products, such as epoxidized FAMES (Campanella et al., 2008)

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Scheme 1. Oxirane ring-opening reaction of epoxidized vegetable oils.

and, also, lubricants (Moser and Erhan, 2008; Moser et al., 2007a,b; Moser and Erhan, 2007). Moser et al. (2007, 2008) have recently been producing branched chain derivatives, partially hydrogenated and, also, diesters through the chemical modification of FAMES and fatty acids.

In this work we propose different synthesis alternatives that can be carried out prior to the esterification step (reaction with an acid anhydride). Several epoxidized vegetable oils obtained from temperate climate crops (soybean, sunflower and high-oleic sunflower oil) were used for the production of polyols. Two types of 'degradation' reactions of the epoxide group were studied (Scheme 1). In the first approach, we employed glacial acetic acid (i.e., in organic phase exclusively), whereas the second reaction involved the opening of the oxirane ring with a short-chain aliphatic alcohol (methanol and ethanol) in aqueous, acid media. Only epoxidized soybean oil was used in the second study. Various thermal (differential scanning calorimetry, DSC) and rheological characterization studies were performed with the VOs, their epoxides and polyol derivatives, to evaluate each natural oil and the impact of introducing chemical modifications – the results of which expand the available database on these novel products.

2. Methods

2.1. Materials

Well-refined, edible quality (i.e., degummed, neutralized, bleached and deodorized) sunflower oil (Natura brand, from Aceit-

Table 1
Main fatty acid composition and iodine values (IV) of the vegetable oils used.

Oil	Fatty acids (wt.%)				IV
	Total saturated	Unsaturated			
		Oleic	Linoleic	Linolenic	
Soybean oil (SBO)	12.1	21.3	59.8	6.80	130
Sunflower oil (SO)	6.5	23.5	67.5	0.50	128
High-oleic sunflower oil (HOSO)	6.46	86.9	6.64	0.00	84

Table 2
Reaction conditions and final epoxide content in the oxirane ring-opening reaction with glacial acetic acid (base reagent: epoxidized soybean oil).

Run	T (°C)	[AA] ^a (M)	Initial AA/epoxide groups molar ratio	Total duration (min)	Final content of epoxide groups ^b (wt.%)	Final conversion ^c
A1	70	12	12.5	1200	0.68	90.08
A2	80	12	12.5	660	0.094	98.63
A3	90	12	12.5	360	0.036	99.46
A4	70	14	16.8	840	0.10	98.53
A5	70	8	4.2	2085	0.086	98.73

^a Initial molarity of acetic acid, [AA]^a = mol AA/l of total volume of the reacting system.

^b Final weight percent of the epoxide groups in the organic phase (% Ep_{final}).

^c The conversion of the epoxide group was calculated as: [(% Ep_{initial} - % Ep_{residual})/% Ep_{initial}] × 100. The initial weight percent of epoxide (% Ep_{initial}) in the organic phase was 6.78 (This is equivalent to 0.42 mol of epoxide per 100 g of epoxidized soybean oil).

era General Deheza S.A., Córdoba, Arg.) and high-oleic sunflower oil (Ecoop brand, from SEDASA, Buenos Aires, Arg.) were used as received. Crude soybean oil (from Oleaginosa Humboldt, Santa Fe, Arg.) was refined in our laboratory. The main fatty acids composition of the oils was determined by gas chromatography (GC) after derivatization of the triglycerides to fatty acid methyl esters, following the AOCS Official Method Ce 1e (Official Methods and Recommended Practices of the American Oil Chemists' Society – AOCS, 1997). The iodine value was also determined using the AOCS protocol, Official Method Da 15-48 (Table 1).

Reagents used in the synthesis and/or preparation steps were glacial formic and acetic acids (acs, 99.81%), fluoroboric acid, HBF₄ (acs, 50%), p.a. grade methanol, ethanol and benzene and 50 wt.% hydrogen peroxide, all purchased from Fisher Scientific (Pittsburgh, PA). Water was doubly distilled (DD) and deionized.

2.2. Preparation of the epoxidized vegetable oils

Stocks of epoxidized soybean oil (ESBO), epoxidized sunflower oil (ESO) and epoxidized high-oleic sunflower oil (EHOSO) were prepared by reacting each VO with performic acid generated *in situ*, at low temperature (20–40 °C), using benzene as a diluent of the organic phase to lower viscosity and minimize ring opening (Gan et al., 1992). The chosen molar ratio of hydrogen peroxide/formic acid/double bonds of the oils was 20/2/1. The VOs, benzene and formic acid were jointly placed into a well-stirred, round-bottom glass reactor kept at 20 °C and then dilute H₂O₂ (30 wt.%) was added dropwise. The reactor temperature was then slowly raised to 40 °C, to complete the reaction (≈20 h). The mixtures were next washed with distilled water until complete removal of performic and formic acids from the organic phase was achieved, and then with NaCl (5 wt.%). Finally, water and benzene were separated from the epoxidized oils in a rotary evaporator. Oxirane and hydroxyl values of the oils were analyzed using AOCS recommended practices, methods Cd 9-57 and Tx 1a-66, respectively.

2.3. Oxirane ring-opening reactions with glacial acetic acid

Each of the epoxidized oils was first used to study the epoxide ring-opening with glacial acetic acid. These reacting systems feature a single, organic phase (Zaher et al., 1989; Campanella and

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