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Epoxidation of Soybean Oil

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ABSTRACT

Soybean oil containing 26% oleic acid, 7% Linolenic, 4% Stearic, 11% Palmitic and 52% linoleic acid, was epoxidised with hydrogen peroxide as oxygen donor,carrier in presence of catalytic amount of an formic acid. Vegetable oils are used as polymerizable monomers in a radiation curable system due to their environmentally friendly character and low cost when compared to products from petroleum. To produce epoxidized soybean oil (ESO), the epoxidation was carried out by conventional chemistry at 50^{o}C, speed of 550 RPM, and atmospheric pressure for about 10 h. An excess amount of hydrogen peroxide was necessary in the reaction to achieve high reaction conversion. A possibly undesirable side reaction was reaction of the epoxy ring opening resulting in hydroxyl functional groups observed by Fourier Transform Infrared Spectroscopy (FTIR). The highest epoxy content of ESO produced had 6.1% (wt). This project hopes to help Iran to start producing vegetable oil-based epoxy ourselves.

Keywords: Epoxidation, Epoxy, Environmentally friendly, Soybean oil

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INTRODUCTION

As energy demands increase and fossil fuel reserves are limited, there has been a growing interest in the utilization of renewable resources as an alternative to petroleum-based polymers. Consequently, much attention has been focused on the development of polymeric materials from vegetable oils, a sustainable resource [7, 8]. Vegetable oil, which is readily available and is a comparatively inexpensive material, can be used to synthesize various types of polymers. Today, one of the most important epoxidized vegetable oils is epoxidized soybean oil (ESO), and its worldwide production is about 200,000 t/year [2]. Several derivatives of vegetable oils are used as polymerizable monomers in a radiation curable system due to their environmentally friendly character and low cost when compared to products from petroleum. Moreover, the long fatty acid chains of vegetable oils impart desirable flexibility and toughness to some brittle resin systems such as epoxy, urethane and polyester resins [4].Triglyceride oils are one of the most important sources for biopolymers. Triglycerides from plants, such as soy bean, palm, rapeseed or sun flower, can be utilized. Triglycerides are composed of three fatty acid chains joined by a glycerol center, with a typical structure shown in Figure 1.

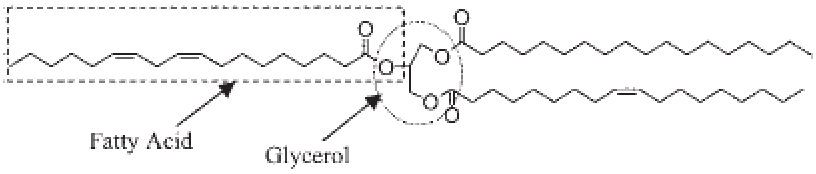


Figure 1. Molecular structure of a typical triglyceride molecule.

Soybean and epoxidized corresponded oils play the key role in comparison with other plant oils due to huge amounts of worldwide productions, low costs and easier conversion to the polyols by ring opening of three membered oxirane groups [11]. Vegetable oils have a number of excellent properties which could be utilized in producing valuable polymeric materials such as epoxy, poly ester amide, alkyd and polyurethane, in addition to its many application in other areas[12]. Fatty acid composition of soybean oil is given in Table 1.1. Soybean oil consists of approximately 15% saturated fatty acids that have no carbon-carbon double bond. Most fatty acids (85%) in soybean oil are unsaturated. The highest percentage of fatty acid in soybean oil is linoleic acid, followed by oleic, palmitic, linolenic, and stearic acids[6]. Linolenic acid contains three double bonds, linoleic acid contains two double bonds and oleic acid contains one double bond. The double bonds in 6 unsaturated fatty acid make these fatty acids susceptible to oxidation, which leads to the development of an off flavor. Thus, they are also the functional group for the following reaction.

There are four known technologies to produce epoxides from olefinic type of molecules: [a] epoxidation with percarboxylic acids [1], the most widely used in industry, can be catalyzed by acids or by enzymes [5,11]; [b] epoxidation with organic and inorganic peroxides which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal catalyzed epoxidation [9]; [c] epoxidation with halohydrins , using hypohalous acids (HOX) and their salts as the reagents for the epoxidation of olefins with electron deficient double bonds [1]; and [d] epoxidation with molecular oxygen [1]. We have used the second method (b) for testing. The project hopes to give a good start to producing (not importing) epoxidized vegetable oil-based materials in Iran.

Table 1.1: Fatty acid composition of soybean oil

Soy Fatty Acid	Structure			%
Unsaturated	Palmitic	CH3(CH2)14COOH	C 16: 0	11
	Stearic	CH3(CH2)16COOCH3	C 18: 0	4
Saturated	Oleic	CH3(CH2)7CH=CH(CH2)7COOCH3	C 18: 1	26
	Linoleic	CH3(CH2CH=CH)2(CH2)7COOCH3	C 18: 2	52
	Linolenic	CH3(CH2CH=CH)3(CH2)7COOCH3	C 18: 3	7

MATERIALS AND METHODS

2.1. Materials

Soybean oil was purchased from a soybean Co ,Golestan, Iran. Formic acid (98%) and Hydrogen Peroxide (30%) were used as reagents in the epoxidation reaction. Acetic acid (Glacial), Crystal Violet and Hydrobromic acid (0.1N in acetic acid) were used in the titration method for determining percent of epoxy.

2.2 Method

2.2.1 Epoxidation of Vegetable Oils

At first, Soybean oil and formic acid were poured to a glass and mechanically stirred and the temperature controlled then, the glass was fixed by a metal clamp in a Benmary (water bath) with water temperature of 50 ^{0}C± 2 and speed of 550 RPM. To start the epoxidation, Hydrogen Peroxide solution (30 %) was gradually charged into the mixture during the first 5 h of reaction. mole ratios of carbon double bonds to Hydrogen Peroxide (C=C:H2O2) were used; 1:1.7 After charging H2O2 was completed, the reaction continued by mixing and controlling the temperature at 50^{o}C for a further 5 h. After that, the mixture was cooled down and neutralized by water. Diethyl ether was used to enhance the separation of the oil product from water phase. The final product was dried out by heating less than 50 ^{o}C. Three replications were performed concurrently. The production procedure of ESO is shown in Figure 2.the double bonds are one of the active sites that can react with functional groups. Epoxy groups react with double bonds in an epoxidation reaction to from epoxidized soy oil.

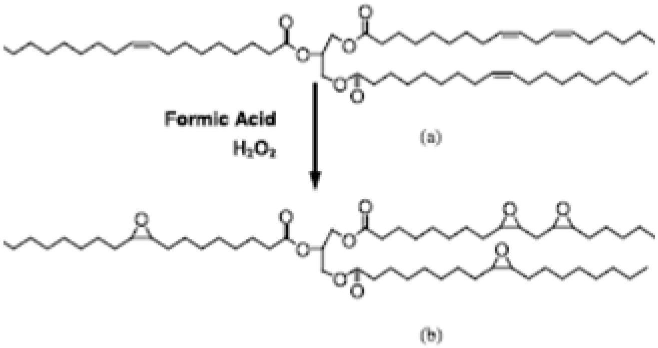


Figure 2.production procedure for ESO: (a) triglyceride molecule, (b) epoxidized soybean oil (ESO)

2.2.2 Analytical Methods

Titration of epoxy (oxirane oxygen)

Epoxy content is the most important property of epoxy materials. Dry epoxidized samples were analyzed for their percents (by weight) of epoxy functional groups by an official method AOCS Cd 9-57 (Oxirane Oxygen in Epoxidized Materials)[3]. Moreover, the following equation was used to calculate the epoxy functionalities of ESO where the molecular weights of ESO are approximately 1000.

$$\%epoxy = \frac{v \times n \times 1.6}{w_m}$$

V: consumed Titrated solution
n: normalized value
w_m: used amount of epoxidized oil

2.2.3 FTIR spectrum

Functional groups of dry epoxidized samples were observed by using Fourier Transform Infrared Spectroscopy (FTIR).Samples were delivered to the Scientific Equipment Center (SEC), Golestan University, Iran, where the analytical services are provided.

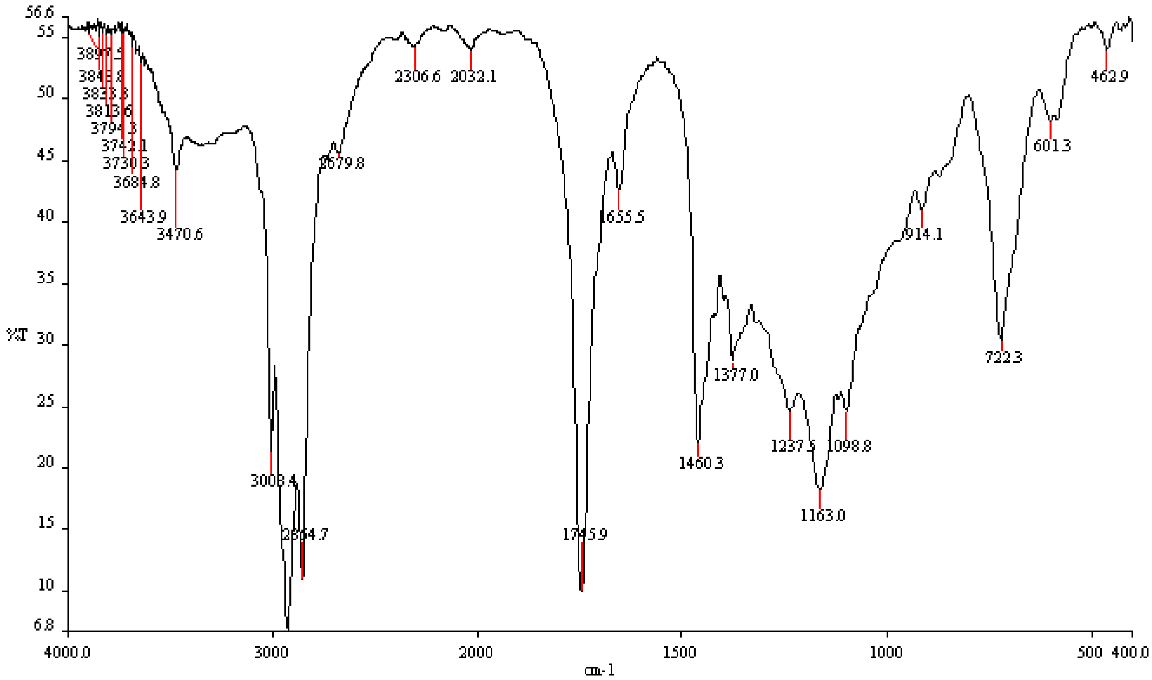
RESULT AND DISCUSSION

3.1 Epoxy Contents of ESO

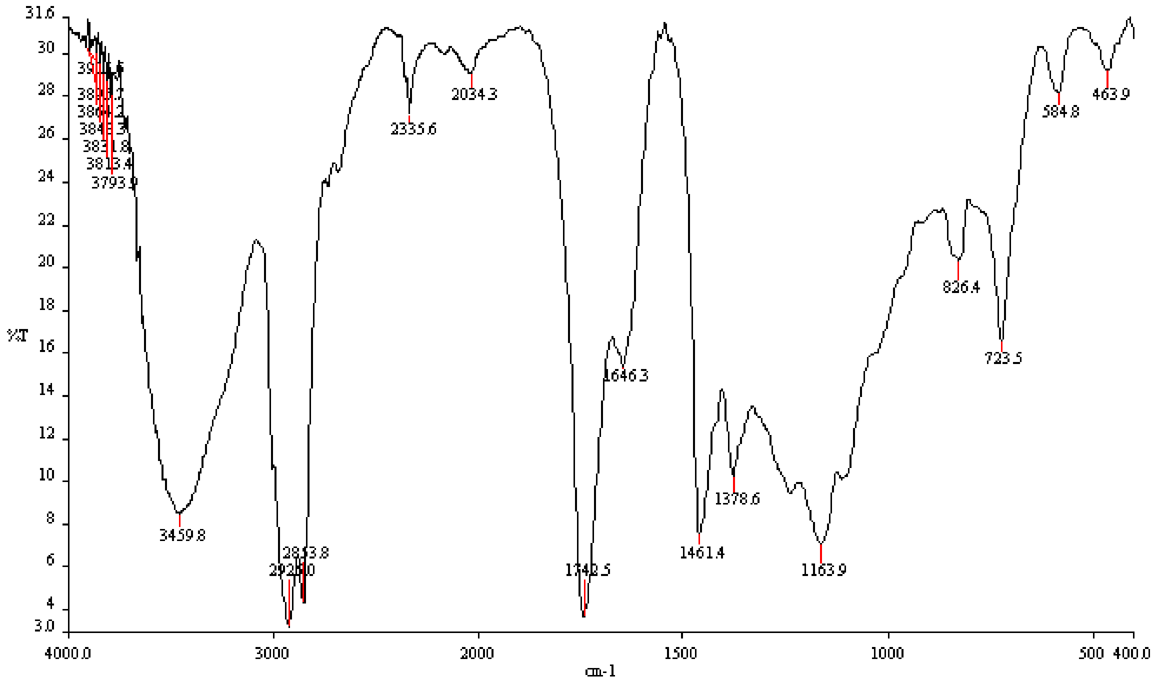
Epoxy content is the most important property of epoxy materials. The highest epoxy content of ESO produced was 6.1%. The fully epoxidized figure was not achieved because there might be some side reaction such as epoxy ring opening which will be discussed in the section of FTIR results.

3.2 FTIR of Triglycerides and Epoxidized Triglycerides

Soybean oil and ESO (with 6.1% epoxy content) were analyzed by FTIR to observe their functionalities. Figure 3 shows FTIR spectrum for these products.



(a)



(b)

Figure 3: FTIR spectrum of soybean oil (a),ESO (b) to show functionality available in raw materials and products of the epoxidation.

The presence of new peak in the FTIR spectra of ESO at 826.4 cm^{-1}, attributed to epoxy group, corroborated the conclusion that the success of the epoxidation reaction of SBO. The other new peak at 3459.8 cm^{-1} was attributed to the hydroxyl O–H stretching, indicating that the epoxy group might be opened.

CONCLUSION

A possible side reaction was the epoxy ring opening that produced hydroxyl functional groups found by FTIR analysis. The highest epoxy contents of ESO were found to be 6.1% (by wt.). There is a possibility of producing ESO in Iran because soybean oil is produced locally.

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