



Development of Radiation curable surface coating based on soybean oil.

Part I. Preparation and characterization of acrylated oil.

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Abstract

An epoxy acrylate was synthesized from epoxidized soybean oil (ESOL) by using acrylic acid monomer. Triethyl amine (TEA) and hydroquinone were used as catalyst and inhibitor respectively. The epoxidized soybean oil acrylate (ESOLA) is done by introducing acrylic acid into oxirane groups of the epoxidized oil (ESOL). This reaction was confirmed by analytical data in terms of oxirane oxygen content, acid value, viscosity and spectroscopically analysis.

Introduction

Epoxy acrylate resins are widely used for protective coatings due to the strong adhesion and corrosion protection of metal ⁽¹⁾. Also, the acrylated epoxies can be hard and chemically resistance if derived from bisphenol A or soft and rubbery if derived from a long chain aliphatic diglycidyle ether ^(2, 3). Soybean oil fatty acid was used to synthesize the modified acrylic coating by esterfication reaction ⁽⁴⁾. Epoxidized palm oil products acrylate (EPOLA) was used as coating on wood substrates ⁽⁵⁾. A



new product from palm oil derivatives by compatibility of epoxidized palm oil with cycloaliphatic diepoxide and using it as a surface coating⁽⁶⁾. Also, an acrylic resin modified by vegetable oil with high degree of unsaturation level was synthesized⁽⁷⁾.

Therefore, the present work, high molecular weight of acrylate polymer has been prepared from soybean oil and acrylic acid.

Analytical data was carried out to illustrate the occurrence of acrylation process.

Materials, methods and techniques

Materials

-Soybean oil: - Pure soybean oil having an iodine value of 130 was used, supplied by paint and chemical industry (PACHIN), Egypt.

-Hydrogen peroxide: - Chemically pure grade; its strength 30%, supplied by El Naser pharmaceutical chemical Co., Egypt.

-Dowex 50W-8X (20-50 mech): - A sulphonated poly (styrene-divinyle benzene) copolymer, dark yellow solid particles and product of Dow Chemicals LTD., England.

- Hydroquinone and Trietheyle amine - Pure (99%), are supplied by Prolabo (France).

-Monomers: - Acrylic acid was supplied by Merck Co. 99%, Germany.

Methods and Techniques

1. The Preparation of Epoxidized Soybean Oil⁽⁸⁾ (In-Situ Epoxidation)

Procedure

The soybean oil was mixed with the required amount of acetic acid (one mole / double bond) and the required amount of catalyst (Dowex 50w-8x) was added together with benzene (as inert solvent). The flask is heated by means of temperature controlled water bath. A moderate



regular stirring is applied during the preparation. When the temperature of the reaction reaches 70 °C, the calculated amount of hydrogen peroxide is added drop wise within two hours. At the end of the experiment (after about four hours), the reaction mixture is separated by separating funnel, washed thoroughly with warm distilled water till acid free and then dried in a vacuum oven at 40 °C.

1.1. Determination of Oxirane Oxygen Content

Many techniques have been used for the determination of oxirane oxygen content of epoxidized soybean oil. In the present work oxirane oxygen content was measured by HBr in acetic acid using crystal violet as indicator ⁽⁹⁾.

$$\text{Oxirane oxygen content (\%)} = \frac{L \times N \times 1.6}{W}$$

Where

L: - is the volume of HBr solution,

N: - is the normality of HBr solution and

W: - is the weight of the sample.

2. Preparation of Epoxidized Soybean Oil / Acrylate Adduct ⁽¹⁰⁾

The apparatus used for acrylation of epoxidized soybean oil is consisted of 500 ml three-neck round bottom flask equipped with a mechanical stirrer, a reflux condenser and a separating funnel.

Procedure

A mixture containing (0.2 mol) epoxidized soybean oil, 0.5 % hydroquinone (on the weight of reactants) as inhibitor and 1.0 % triethyl amine (on the weight of reactants) as a catalyst were charged into three-necked flask. While stirring the mixture, (0.8 mol) acrylic acid was



introduced to the mixture through the separating funnel. After the addition of acrylic acid was completed, the mixture was then heated up to (110 °C). The progress of acrylation reaction is followed by measuring the acid value of the mixture. The reaction was terminated when the acid value of the resin reached a value less than 5 mg KOH / gm resin.

The product is washed by using 1% NaH₂PO₄ and 1% NaCl to remove excess acrylic acid.

2.1. Determination of the Acid Value

According to ASTM D 1639-90. The acidity expressed as acid value A.V. is given by the equation

$$A.V. = \frac{N \times V \times 56.1}{W}$$

N: - is the normality of KOH,

V: - is the volume of KOH and

W: - is the weight of the sample.

3. Determination of Solid Content

A designated quantity of coating specimen is weighed in a suitable bettery dish (or crucible) and heated in an oven at 110 ± 5 °C till constant mass.

$$\text{Solid content (\%)} = \frac{W_1}{W_0} \times 100$$

4. Fourier Transform Infrared Spectrometry, (FTIR)

ATI Mattson, Genesis series, Fourier Transform Infrared Spectrometry was used.



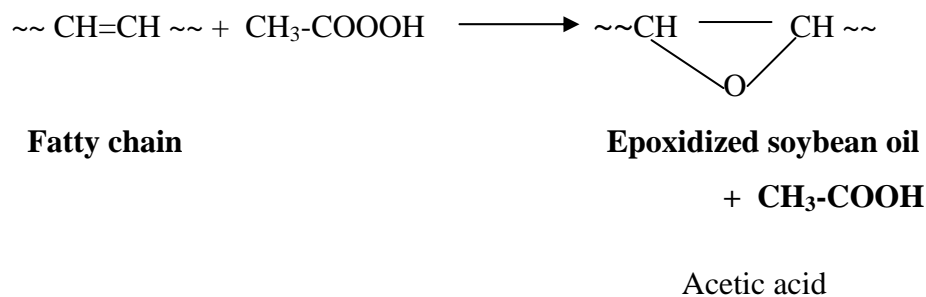
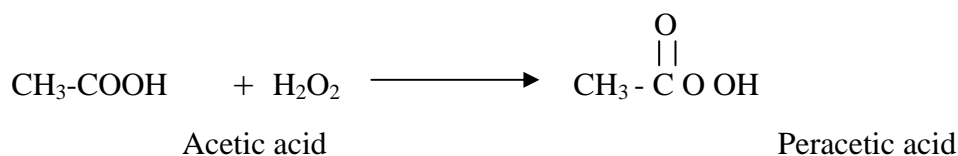
5. Viscosity Measurements

The viscosity was measured by using Programmable Rheometer DV III RV. In the present work, the viscosity of resin was measured at room temperature and at 50 °C.

Results and Discussion

-Preparation of Epoxidized Soybean Oil (ESOL)

Soybean oil was epoxidized by preparing peracetic acid **in – situ** using ion exchange resin (**Dowex 50-8X**) as catalyst.



The oxirane oxygen content of the prepared epoxidized soybean oil was found to be 6%.

- Preparation of Epoxidized Soybean Oil Acrylate



The acrylated epoxidized soybean oil (ESOLA) is subjected to the acrylation process. The epoxy group of the epoxidized soybean oil may react with acrylic acid to produce epoxidized soybean oil acrylate (ESOLA). The acrylated epoxidized soybean oil molecules will contain double bond and hydroxyl groups. Thus, the acrylated oil can be polymerized via double bonds. This means that, adhesion and wetting with pigments of fillers will be improved due to the presence of the hydroxyl groups ⁽¹¹⁾.

The blend of oil and triethyl amine was heated to 80 °C with moderate continuous stirring. The colour of the above mentioned blend was changed from light yellow to dark yellow to brown colour due to the formation of a complex between triethyl amine and epoxidized soybean oil (ESOL).

When the temperature in the reaction flask was steady at 80 °C, the calculated amount of acrylic acid was introduced to the oil blend via a separating funnel at a very slow rate. A cloudy atmosphere was observed in the reaction flask due to the evaporation of acrylic acid, but after while, the atmosphere in the flask becomes clear again.

Since the reaction is exothermic, the temperature may be raised above 80 °C. In such case, the heating mantle should be turned off. The colour of the mixture changed from brown to yellow upon the addition of acrylic acid. After complete addition of acrylic acid, the temperature was raised to 110 °C and then maintained until the acid value of the adduct was less than 5 mg KOH /g sample.

It is important to maintain the temperature at or below 110 °C in order to avoid gelation. The stirring rate should be increased as the viscosity of mixture increased. It is important to mention here that gelation is the hindrant factor in the synthesis of epoxy acrylate adducts. Two factors should be taken into consideration during preparation of the



epoxy acrylate adducts; they are: the rate of addition of acrylic acid, must be very slow, and the reaction temperature should not be exceed 110 °C.

In this work the synthesis was terminated, when the acid value reached 10 mg KOH/gm resin. The product was a very viscous acrylic prepolymer and dark yellow in color. Also, the solid content of the resin was found to be 99.2 %. The obtained product was characterized chemically by measuring oxirane oxygen content, acid value, viscosity and spectroscopically by IR.

Table (1) shows the progress of acrylation process by determination of acid values (A.V.) intervally. From table (1), it can be notice that, the initial acid value of the starting sample mixture after adding acrylic acid is 108 mg KOH / gm resin. After acrylation process, the acid value of epoxy acrylate was 10 mg KOH / gm resin through 40 hours. Therefore, the acid values of epoxidized soybean oil acrylate have decreased by a value of about 98 mg KOH /gm resin due to the acrylation of oil and the reduction of free acrylic acid content in the mixture resulted in a subsequent increase of acrylate groups in the backbone triglyceride molecules.

The analytical data of ESOL, ESOLA and washed ESOLA are given by table (2).

Table (2) shows that, the oxirane oxygen content of ESOLA and washed ESOLA are 0.1% and 0.15% respectively compared with 6% found in the starting material ESOL. This means that almost all oxirane oxygen has participated in the reaction to yield ESOLA.

On the other hand, due to the viscosity of epoxy acrylate adduct is very high, it is difficult to measure at room temperature by normal viscometers, but, it is found that the viscosity start to be recorded by increasing the temperature up to 50 °C. By the comparison between ESOL and ESOLA resin at room temperature and at 50 °C, it is interesting to notice that, the increase of the viscosity of epoxidized



soybean oil acrylate may be due to the increase of molecular weight, high branching and / or hydrogen bonding.

Table (1): A.V., mg KOH per gm resin after addition of acrylic acid at different times.

Time (hours)	Acid value of epoxy acrylate (ESOLA)
Before reaction	108
5	73.8
10	60
14	52.7
20	38
24	28
29	22.2
33	16
37	10
40	10
After washing	1.5

Table (2): Analytical data of ESOL, ESOLA and Washed ESOLA

Properties	ESOL	ESOLA	Washed ESOLA
Oxirane oxygen content, % per mole.	6	0.1	0.15



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Acid value, mg KOH/gm resin	1	10	1.5
Viscosity, cps at room temperature 25 °C	464	Very high viscosity	Very high viscosity
Viscosity, cps at 50 °C	106	—	6700

Also, the acrylation reaction can be detected by IR-spectra for epoxidized oil and epoxy acrylate resin as shown in figures (1, 2) respectively. Figure (1) shows a peak at 824 cm^{-1} which represent oxirane groups in the triglyceride molecule. Whereas a weak band representing hydroxyl groups can be shown at 3476 cm^{-1} , this might be due to the presence of acid residue during ESOL preparation. On the other hand, the reaction between epoxidized soybean oil and acrylic acid has been taken via the three functional groups. This is very clear in figure (2), where the peaks of the epoxy groups have been diminished while other two bands have been appeared. These new bands which appears at 1619 cm^{-1} may be attributed to the acrylate group ($\text{CH}_2=\text{CH}-\text{COO}-$), while the other broad band which appear at 3489 cm^{-1} may be attributed to (-OH) group ⁽¹²⁾. This means that almost all the epoxy groups have been consumed during the acrylation process.

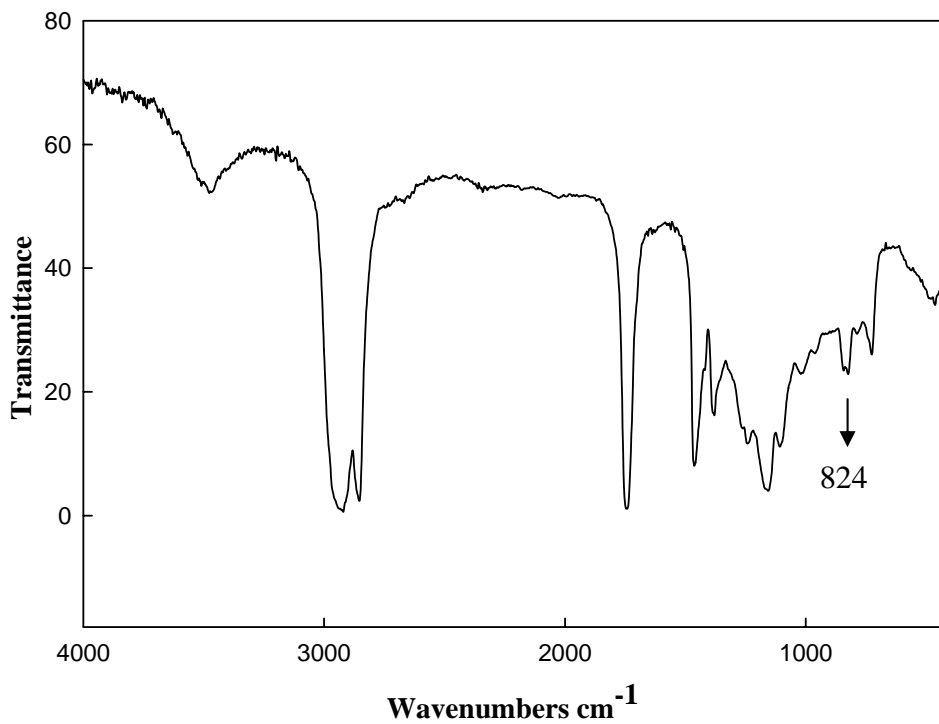


Figure (1): IR spectra of epoxidized soybean oil

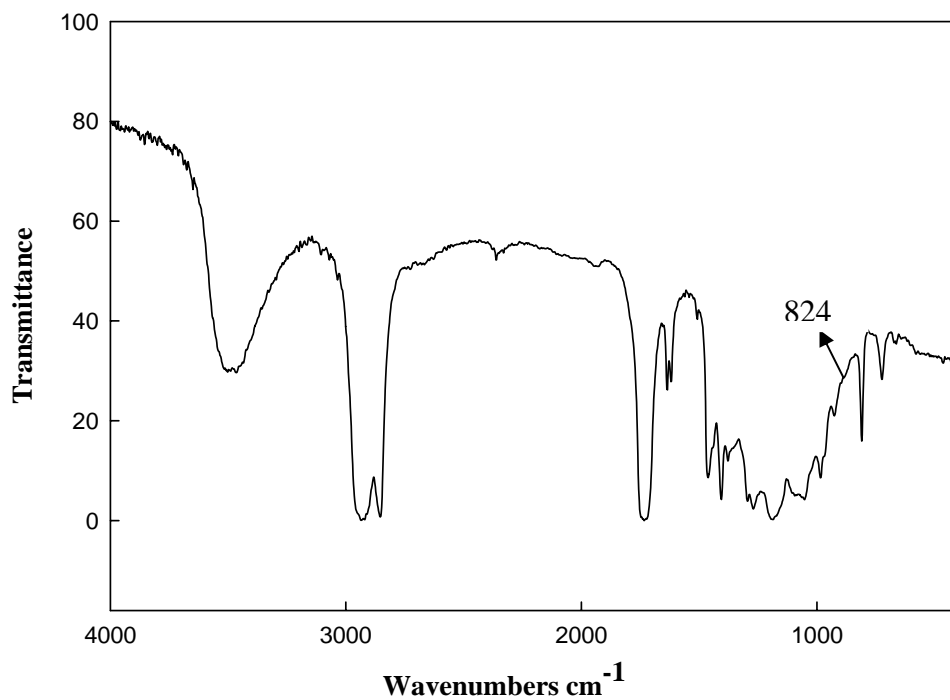


Figure (2): IR spectra of epoxidized soybean oil acrylate

The above measurements may lead to the following mechanism for the acrylation process of epoxidized soybean oil using triethyl amine as catalyst as in figure (3).

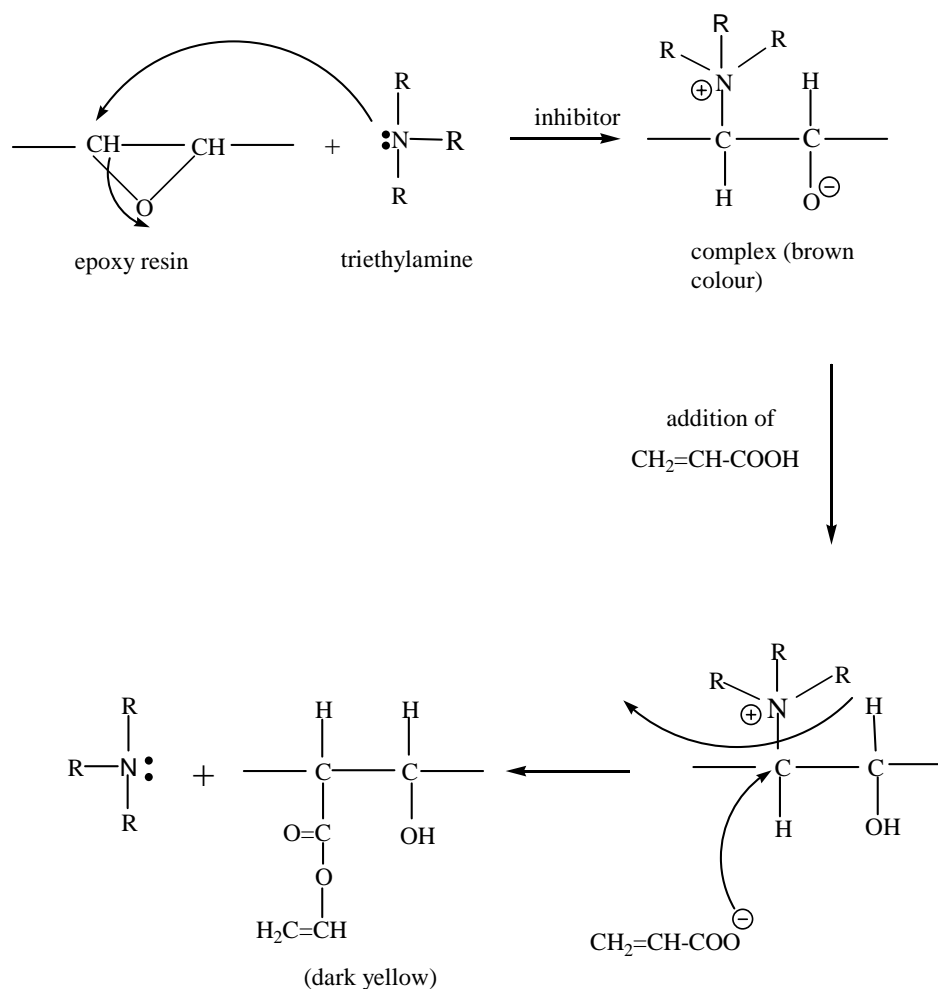


Figure (3): Mechanism of acrylation reaction



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