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RESEARCH OF VEGETABLE OIL EPOXIDATION

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Abstract: This paper investigates the epoxidation of sunflower oil. The interaction of epoxidation and its derivatives with formic acid and hydrogen peroxide was studied. Also, during the epoxidation process, 50 g of sunflower oil and 7 g of formic acid were added to the flask, the glass was slowly heated while stirring at a speed of 200 rpm, and after 30 minutes, 15 g of 30% hydrogen peroxide was added. The temperature was maintained at 70°C for 3 hours. The composition and structure of epoxidized sunflower oil were studied and analyzed using modern IR- spectrum, Raman spectrum, NMR, and PMR methods.

Keywords: Sunflower oil, epoxidation, formic acid, hydrogen peroxide, IR- spectrum, Raman spectrum, NMR and PMR.

Vegetables oils are a sustainable and renewable raw material resource extracted from plants and wood. These vegetables oils are used like starting material and they offers numerous advantages such as low toxicity and inherent biodegradability. In the last years, the epoxidation of vegetables oil received a great interest from industry [1]. Epoxidation is a reaction widely used to form oxirane rings from ethylenic unsaturations (C=C) [2]. The cyclical structure of oxirane rings has a bond angle of 60 °C, making them highly strained and highly reactive [3]. Classic methods employed for the oxidation of vegetable oils use homogeneous catalytic processes that generate a lot of waste, corrode equipment and require large amounts of reagents. Heterogeneous catalysts have the advantage of easy separation and recycling of the catalyst. For this reason, ion exchange resin has been studied to promote epoxidation of vegetal oils [4]. Biobased metal cutting fluid (MCF) is an important material that has wide use in industry as a substitute for cutting fluids based on fossil-derived hydrocarbons [5]. MCFs can be made from vegetable oils, but some oils have low stability, mainly at high temperature. To solve this problem, epoxidation reactions are applied to convert unsaturations to oxirane rings followed by opening of the rings with water, to form the vicinal diol [6,7]. Several authors have investigated heterogeneous catalysts based on the sulfonation of incomplete pyrolyzed biomass, such as sucrose [8], glucose [9,10] and biochar [11]. Conventionally, the production of epoxidized vegetable oils is carried out by the Prileschajew method [12]. It is a liquid-liquid reaction system, where there are several consecutive and parallel exothermic reactions [13].

Sepulveda et al. [14] tested different alumina catalysts for the epoxidation of methyl oleate and soybean oil methyl ester by hydrogen peroxide in different organic solvents. They reached a conversion of ca. 100%, Di Serio et al. [15] tested Nb₂O₅-SiO₂ catalyst for the epoxidation of soybean oil in organic solvents, but the selectivity was quite low, Turco et al. [16] studied the epoxidation of soybean oil and methyl oleate with hydrogen peroxide on γ -alumina in the presence of different organic solvents. They have demonstrated that the solvent plays an important role for this system. They have reported that acetonitrile was the best solvent for the epoxidation of methyl oleate, Parada Hernandez et al. [17] have studied the system H₂O₂/alumina/ethyl acetate for the epoxidation of methyl ricinoleate. They demonstrated that this system is efficient for the epoxidation of this oil.

In the present study, epoxidation and ozonolysis led to a decrease of 40.8 and 51.9 % in the degree of unsaturation of corn oil, respectively[18]. Epoxidation of flax oil in a conjugate system with hydrogen peroxide using chlorinated cation exchanger KU-2×8 as catalyst was studied. The influence exerted on the epoxidation rate and target product quality by the temperature, stirring intensity, catalyst amount, and reactant ratio was examined[19]. This study presents epoxidizing podocarpus falcatus seed oil through epoxidation reaction by using synthesized solid sulfonated silica catalyst from locally available sugarcane bagasse ash[20]. Some of them are play an important role as corrosion inhibitors for technological tools[21-25].

Renewable resourced polymer composites from vegetable oils and bio-fibers are receiving increasing attention from various industries due to their characteristics of being less heavy, environment friendly, and biodegradable. Lignocellulosic natural fibers have immense potential to be used as reinforcing fillers due to their characteristics of being less expensive, abundant obtainability, lower density, higher specific strength and modulus, and good interfacial strength with thermoset polymers. In this chapter, epoxidized nonedible linseed and castor oils are proposed as a diluent to petro-based epoxy in formulating toughened bio-based copolymers. Unidirectional sisal fibers were reinforced within a network of such bio-epoxy copolymers in order to achieve an optimal stiffness–toughness balance. Cardanol based phenalkamine, a bio-renewable crosslinker, is used to develop well toughened sustainable and green composite materials. The composites were subjected to various thermal, mechanical, dynamic mechanical, and morphological tests to investigate the impact of nonedible epoxidized oils and sisal fibers in addition to the petro-based epoxy matrix. The present study shows the method for design and development of novel sustainable green composites with higher bio-source content (>65%) meant for shock absorbing applications[26].

2. Materials and Methods: Sunflower oil according to GOST 1.2-2009 and formic acid according to GOST 1706-78 are used in the experiment. For this, 50 g of sunflower oil and 7 g of formic acid were added to the flask, the glass was slowly heated while stirring at a speed of 200 rpm, and after 30 minutes, 15 g of 30% hydrogen peroxide was added. The temperature was maintained at 70°C for 3 hours. 4 g of hydrogen peroxide was added. Then, after 3 hours, hydrogen peroxide was added to the reaction mixture and stirred again. The resulting mixture was cooled, washed with 5% sodium bicarbonate aqueous solution, and separated in a separatory funnel. The organic phase was washed with distilled water. The water mixed with the organic phase is separated by vacuum and the oil is dried. The iodine number and epoxide number of the obtained epoxidized oil are determined. The resulting mixture was cooled and CO₂ gas was passed while heating in an oil bath by adding 5 grams to a test tube, the process was carried out in the presence of a catalyst. The process of epoxidation of formic acid, as well as large-ton vegetable oils: sunflower oil, was studied. Oxidation was carried out using hydrogen peroxide, and tetra butyl titanate catalyst, which were obtained using the appropriate concentrated acids and an aqueous solution of hydrogen peroxide. Oxidation kinetics was assessed by an accumulation of peroxide compounds, iodine value, and number.

3. Results and Discussion: 3.1. The IR spectrum of epoxidized sunflower oil. IR-spectrum ("IR Tracer-100" SHIMADZU CORP., Japan, 2017) analysis of the substance obtained as a result of the reaction was carried out. As can be seen from Figure 1, the presence of a plane (=C-H) and a ring (C=C) at 1506 cm⁻¹, the presence of a strain vibration (-C-H) at 1230 cm⁻¹, and a deformation vibration at 1031 cm⁻¹ (-O-CH₃) 771 cm⁻¹ (CH-O-CH-) was found to be present. The presence of bonds belonging to the (-C=C-) group in the 1581.63 - 1606.7 cm⁻¹ area, the presence of a stretching vibration in the 1182.36 - 1296 cm⁻¹ area (C-C-C), 1361.74 cm⁻¹ The presence of bonds in the areas (-CH₂-CH₂-) indicates the composition of the original substances, the presence of bonds in the area

1456 cm^{-1} (-O-CH₂-), the presence of an epoxy group in the areas 2966.52-3055.24 cm^{-1} proves that sunflower oil is epoxidized (1 -picture).

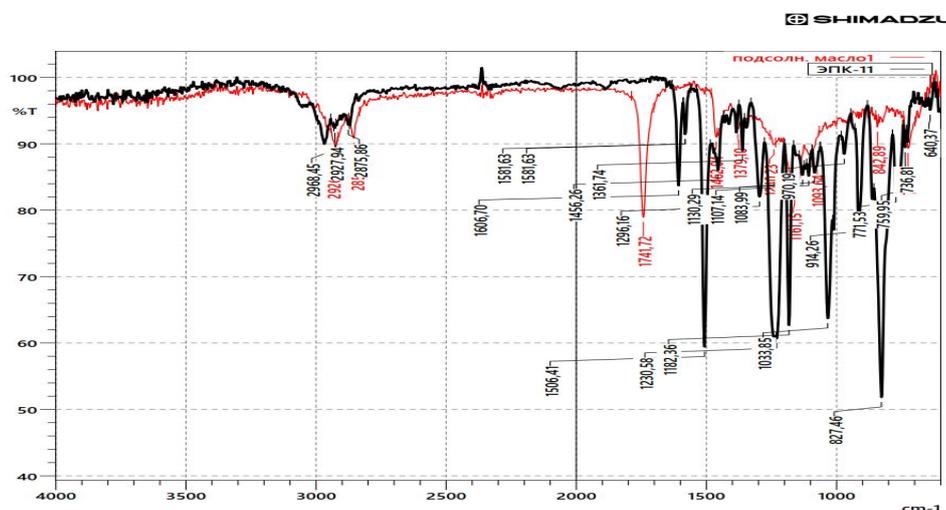


Fig 1. IR-spectrum of epoxidized oil based on sunflower oil.

3.2. Roman Spectroscopy. Analysis. In the following a picture, Raman spectrum analysis of epoxidized sunflower oil was carried out. According to the results of the analysis, the vibrations of the C-H groups at the absorption frequency of 3078 cm^{-1} at the frequency of 2929-1989-1694 cm^{-1} are the branches of the CH₂ and CH₃ groups, and the presence of absorption bands in the region showed that this is not observed in non-epoxidized oil. 1183-1290 cm^{-1} and 667-821 cm^{-1} (CH-O-CH-) were studied to be present in the absorption zone in the region, characteristic of the vibrations of methylene groups, due to the increase in its intensity, the process is active oxygen released as a result of the decomposition of hydrogen peroxide. The progress of oxidation reactions under the influence showed that it is epoxidized.

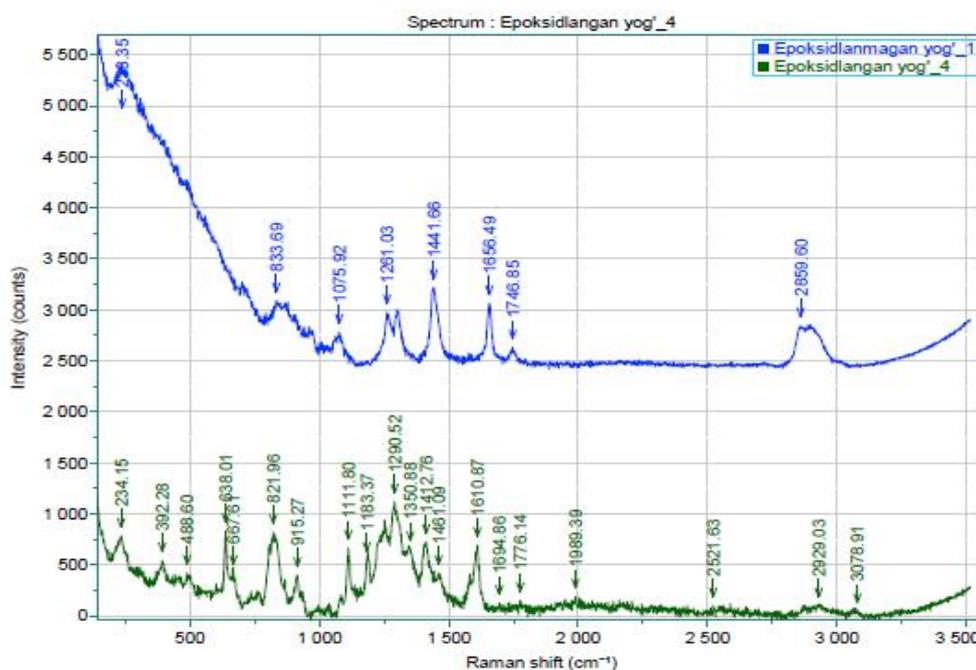


Fig. 2. Roman spectrum of epoxidized oil based on sunflower oil

3.4. The iodine number of epoxidized sunflower oil was determined. The results are presented in Table 4. The iodine number (x) was calculated according to the following formula: $X = ((A-V),75:100)/(0.1:1000)$ (1.1). Here, A is the volume of the alcohol control solution of iodine used for titration; ml. B - the volume of an alcohol solution of iodine used for experimental titration; ml. 0.75 g - a mass of iodine corresponding to 200 ml of 0.05% alcohol solution of iodine; 100 - recalculation to 100 g of oil; 1.3 - the weight of oil in grams; Conversion factor of 1000 mg of iodine to grams.

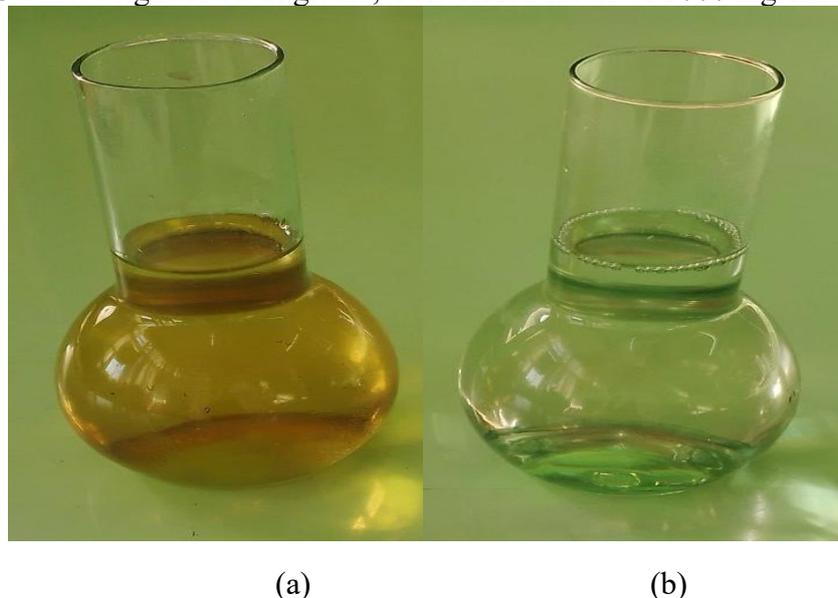


Fig. 4. Initial state of sunflower oil (a) epoxidized state of sunflower oil (b).

Table 2. Determination of iodine number of epoxidized sunflower oil

System components and conditions	Number of iodine
Sunflower oil	124,6
Oil + hydrogen peroxide + formic acid + sodium bicarbonate (aqueous solution) + carbon dioxide gas 3h, 70°C	117,8
Oil + hydrogen peroxide + formic acid + sodium bicarbonate (aqueous solution) + carbon dioxide gas + tetramethyl ammonium bromide 24h, 140-150°C	117

From Table 2, we can see that when sunflower oil is studied as a sample, its iodine number is equal to 124.6, and when it is processed, these indicators decrease. When vegetable oil was treated with hydrogen peroxide, formic acid, an aqueous solution of sodium hydrogen carbonate, and carbonic anhydride, it was found that the number of iodine in it changed to 117.8. When the effect of the catalyst on processed vegetable oil was studied, it was found that the number of iodine in it is equal to 117. As a result of the conducted scientific research, it can be said that after processing the vegetable oil, its iodine content was reduced. The method of adding hydrogen peroxide has a significant effect. Because hydrogen peroxide decomposes after 3 hours of practical experience. If an additional portion of hydrogen peroxide was added to the reaction mixture after 3 h, this resulted in a significant increase in product yield.

Table 3. Study of epoxidation process of vegetable oil (reaction time 6 hours at 60°C).

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