

OPTIMIZATION STUDIES ON THE SYNTHESIS AND CHARACTERIZATION OF BIO-BASED EPOXIDIZED SOYBEAN OIL (ESBO)

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ABSTRACT

There is an urgent need to replace petroleum based polymers by way of bio-based polymers. Bio-based polymers help in the reduction of fossil fuels usage, and improve economic and environmental concerns. Further, composites made using them become viable replacements for metal parts in the aerospace, marine, and automotive industries. The major sources for bio-based polymers are vegetable oils, which offer advantages such as being renewable, biodegradable, and abundant. It is the unsaturated double bonds in the vegetable oils that are converted for polymeric materials such as use in coatings and resin systems. Hence, this research focuses on synthesizing a completely bio-based polymer to achieve a high bio-content via an epoxidation process which uses soybean oil to produce a soybean based epoxy resin. The epoxidation process used in this study uses a chemical method that consists of using soybean oil with unsaturation (double bond) sites, carboxylic acid (formic acid) as the oxygen carrier, and hydrogen peroxide as the oxygen donor in converting the double bonds in the oil to epoxide groups. The desire to obtain high oxirane oxygen content (OOC) (epoxide group) is contingent on obtaining an optimum stoichiometric ratio for control purposes based on certain criteria. These criteria focus on comparing and varying the effect of temperature (at 50 and 60 °C), reaction time (at 2, 4 and 6 hours), and concentration of hydrogen peroxide (at 1, 1.5, and 2 molar ratio). These parameters are monitored to achieve an optimum system that would yield the highest oxirane oxygen content. The determination of the epoxide groups was performed through manual titration process using ASTM D1652-11. The highest percent oxirane oxygen content using formic acid was found to be 7.45, yielding a 98% conversion. Fourier transform infrared (FTIR) spectroscopy and rheology verified the presence of epoxide groups from ASTM D1652-11.

1 INTRODUCTION

Over the past few decades, there has been an ever-growing movement to turn our everyday petroleum based products into completely bio-based products. The reason for this focuses on the vast amount of carbon emissions released in the earth's atmosphere as a result of an all-petrochemical based product. While a completely bio-based product as of right now has not been achieved, manufacturers are adding bio-based materials into petroleum based materials to reduce the amount of carbon emissions and other volatile substances. The addition of bio-based materials used in petroleum based materials is also necessary to maintain a level of mechanical properties, as bio-based materials tend to have lower properties than the petroleum based materials.

One of the most common resins for advanced composite applications is epoxy resin [1]. Epoxy resin has excellent mechanical and thermal properties [2]. The resin also has very good chemical resistance and bonds well with embedded fibers[1]. For these reasons, epoxy resin is a popular resin.

However, most epoxy resins are not eco-friendly nor is it bio-degradable. It is this reason that provides the impetus to synthesize a completely bio-based epoxy resin system from vegetable oils. Vegetable oils are one of the most inexpensive ways to create a resin system. They are sustainable, renewable, biodegradable with low toxicity, and for many of the oils, they are the most abundant biological feedstock available in large quantities [3].

Among all the vegetable oils, soybean oil is the most widely used oil due to its large productions, low cost costs, and easier conversion to the polyols by ring opening of three membered oxirane groups [4]. Most fatty acids in soybean oil are unsaturated, with high percentage of linoleic acid, followed by oleic, palmitic, linolenic, and stearic acids. Linolenic acid contains three double bonds, linoleic acid contains two double bonds and oleic acid contains one double bond. The double bonds in unsaturated fatty acids make these fatty acids susceptible to oxidation.

However, the fatty acids in the oils for conversion to epoxy resin for polymeric use constitutes the unsaturated double bonds by way of an epoxidation process. The epoxidation process uses hydrogen peroxide as an oxygen donor in the presence of formic or acetic acid as an oxygen carrier to form a performic or peracetic acid [5]. This performic or peracetic acid further reacts with the unsaturated bonds of a vegetable oil to produce epoxide groups (or oxirane oxygen content (OOC)) used for crosslinking. Thus, high oxirane content between 5.5 and 7 % is recommended for soybean oil [6]. However, due to different percentages of fatty acids in oils, the physical and physiological properties may vary.

Thus, in order to properly synthesize an epoxidized soybean oil system, this research takes into account varying the effect of reaction time (at 2, 4, and 6 hours), reaction temperature (at 50 and 60 °C), and molar ratios of hydrogen peroxide (at 1, 1.5, and 2 mole ratio) as these are factors that influence the epoxidation reaction. The overall goal is to understand how the oxirane oxygen constant changes as a result of these factors.

2 EXPERIMENTATION

2.1 Materials

Soybean oil in its raw form, formic acid ($\geq 95\%$) and hydrogen peroxide (30 wt. %) used in this study were obtained from Sigma Aldrich. The fatty acid percent composition of soybean oil provided by Sigma Aldrich is shown in Table 1. This oil is estimated to have a total of seven double bonds from oleic, linoleic, and linolenic fatty acids.

Saturated Fatty Acids		Unsaturated Fatty Acids	
Lauric	0.2 %	Palmitoleic	0.4 %
Myristic	0.1 %	Oleic	28.9 %
Palmitic	9.8 %	Linoleic	50.7 %
Stearic	2.4 %	Linolenic	6.5 %
Arachidic	0.9 %	"unknown"	0.1 %

Table 1: Fatty Acid Percent Composition of Soybean Oil

Other materials used in this study consist of sodium bicarbonate, sodium sulfate, and distilled water. These materials were used in the post treatment after the synthesis which included neutralizing and drying to obtain the final product. Additional materials includes acetic acid (glacial), tetraethylammonium bromide (anhydrous), perchloric acid (60 %), acetic anhydride, methylene chloride, crystal violet indicator, and potassium acid phthalate. These materials were all purchased from Sigma Aldrich and used in the determination of the oxirane oxygen content based on ASTM D1652-04.

2.2 Synthesis of Epoxidized Soybean Oil

The synthesis of epoxidized oil followed the procedures found in literature [7, 8] with slight modifications. Soybean oil (1 mole) and formic acid (0.5 mole) were placed in a three-neck flask equipped with a thermometer and magnetic stirrer. The flask containing the solution was submerged in an oil bath on top of a magnetic stirring hot plate. The mixture was stirred at 900 RPM at the desired reaction temperatures and times. The temperature was reduced by 5 °C before the required amount of hydrogen peroxide was added. The reduced temperature was to avoid a drastic temperature rise as a result of the exothermic nature during the addition of hydrogen peroxide. With the temperature reduced by 5 °C, the required amount of hydrogen peroxide was slowly added to the mixture using a titration tube to start the epoxidation reaction. The reaction temperature and time was varied at 50 and 60 °C at 2, 4, and 6 hours. The hydrogen peroxide was varied at 1, 1.5, and 2 molar ratio; thus three different ratios of carbon double bonds: formic acid: hydrogen peroxide of 1:0.5:1, 1:0.5:1.5, and 1:0.5:2 were studied. The prospective synthesis route and its outcome are shown in Figure 1.

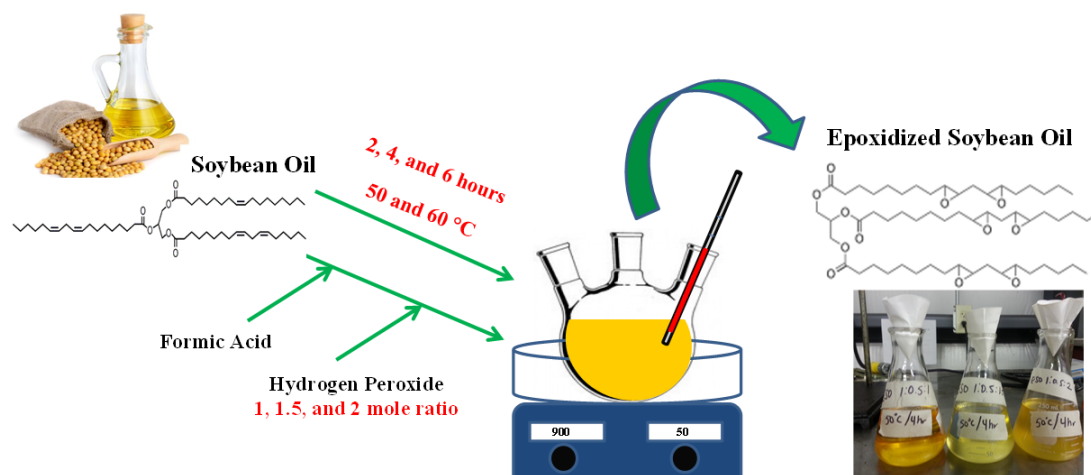


Figure 1: Processing parameters, reactants and end result of the synthesis of epoxidized soybean oil.

After completion of the reaction, the epoxidized soybean oil was allowed to cool to room temperature. Once cooled, the reaction was filtered and washed several times with distilled water to remove any excess formic acid or hydrogen peroxide. Sodium bicarbonate in the amount of 5 wt. % was dissolved in 100 mL of distilled water and used to neutralize the reaction to obtain a pH of 7. This solution was placed in a beaker on a magnetic stirring plate to allow for constant mixing. Finally, the neutralized epoxidized soybean oil was dried over sodium sulfate and placed in an oven overnight at 70 °C.

3 CHARACTERIZATION TECHNIQUES

3.1 Determination of Oxirane Oxygen Content

The oxirane oxygen content is a key parameter that determines the amount of epoxide groups formed during epoxidation. This parameter is calculated according to ASTM D1652-11 that uses a manual titration for determining the oxirane oxygen content. The oxirane oxygen content was found based on two steps.

The first step involves determining the standardization of 0.1 N Perchloric Acid Reagent. In this step, 0.4 grams of potassium acid phthalate was dissolved in approximately 50 mL of glacial acetic acid placed in a glass beaker. Eight drops of crystal violet indicator solution was added to the solution while on a magnetic stirrer, stirring at 240 RPM. Perchloric acid reagent was titrated into the solution, in which the endpoint was achieved once the solution changed from a violet to green color as shown in Figure 2.



Figure 2: Change in Color indicating reaction endpoint.

From this step, the normality of perchloric acid reagent (N) was calculated using equation (1).

$$N = \frac{W \times 1000}{204.2 \times V} \quad (1)$$

Where, W is the amount of potassium acid phthalate used in grams and V is the volume of perchloric acid reagent required to titrate the solution in mL.

The second step involves the actual procedure for testing the epoxidized soybean oil samples. This step requires knowing the expected epoxide equivalent weight (EEW) of epoxidized soybean oil. The EEW of epoxidized soybean oil determines the amount of synthesized epoxidized soybean oil to use in the titration test. From literature, much research relates the EEW of epoxidized soybean oil to be between 170 and 375 [9–11], thus requiring the use of 0.4 grams of synthesized soybean oil to be tested in the titration test. The 0.4 grams of the specimen was added to a glass beaker along with 15 mL of methylene chloride. A magnetic stirrer was inserted into the solution while 10 mL of tetraethylammonium bromide reagent was added. The mixture was stirred at a speed of 240 RPM as eight drops of crystal violet indicator was added. The mixture was titrated using the perchloric acid reagent until there was a change in color from violet to green. The volume of perchloric acid reagent used was recorded and used to calculate the oxirane oxygen content using equations (2) and (3).

$$E = 4.3 \times V \times \frac{N}{W} \quad (2)$$

$$OOC = \frac{16}{43} \times E \quad (3)$$

Where E is the weight percent epoxide, N is the normality found in step 1, and W is the weight of the epoxidized soybean oil used.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Determination of the chemical bonds and structures of the synthesized epoxidized soybean oil were characterized using Fourier Transform Infrared Spectroscopy (FTIR). The Shimadzu FTIR 8400s machine equipped with MIRacle™ ATR was used to obtain an infrared spectrum of absorbed emissions. Each sample was scanned from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . FTIR was used to determine the change in functional groups that contribute to the synthesis of each system, as well as to verify the number of epoxide groups.

3.3 Rheology

Rheological studies were carried out using TA Instruments AR-2000 equipped with environmental testing chamber (ETC) and 25mm parallel plates. Scans were performed at room temperature with varying shear rate from 0 to 300 s^{-1} . This test was used to record the change in viscosity as a function of the shear rate in order to determine processing and performance conditions. The results were further analyzed using TA Instruments Data Analysis software.

4 EXPERIMENTAL RESULTS

4.1 Determination of Oxirane Oxygen Content

The oxirane oxygen content (OOC) determined from the titration method of ASTM D1652-11 is

revealed in Table 2 for the epoxidation reaction using formic acid at varied reaction temperature, reaction time, and molar concentrations of hydrogen peroxide content. Also presented in Table 2 is the epoxide equivalent weight (EEW) and relative conversion to oxirane (percent conversion). Further visual on varying the reaction temperature at 50 and 60 °C, the reaction time at 2, 4, and 6 hours, and the molar concentration of hydrogen peroxide at 1, 1.5, and 2 mole ratios are shown in Figures 3(a) and 3(b). Parameters such as the oxirane oxygen content, relative conversions to oxirane, and epoxide equivalent weight ranged in values from 1.08-7.45, 14-98 %, and 110-765, respectfully with varying temperature, reaction times, and molar concentration of hydrogen peroxide. The determination of the relative conversion to oxirane was compared to the theoretical oxirane oxygen content that was found to be 7.58.

Sample	Epoxide Equivalent Weight (EEW) (g/eq)	Oxirane Oxygen Content	Relative Conversion to Oxirane (RCO), (%)
50°C - 2 hours - 1M	431.25 ± 44.59	1.91 ± 0.20	25.24 ± 2.59
50°C - 2 hours - 1.5M	762.18 ± 13.51	1.08 ± 0.02	14.18 ± 0.25
50°C - 2 hours - 2M	556.48 ± 21.11	1.47 ± 0.06	19.44 ± 0.73
50°C - 4 hours - 1M	217.77 ± 4.18	3.76 ± 0.07	49.64 ± 0.95
50°C - 4 hours - 1.5M	396.21 ± 14.38	2.07 ± 0.08	27.30 ± 1.00
50°C - 4 hours - 2M	259.05 ± 2.06	3.16 ± 0.03	41.72 ± 0.33
50°C - 6 hours - 1M	126.89 ± 1.53	6.46 ± 0.08	85.18 ± 1.03
50°C - 6 hours - 1.5M	116.22 ± 0.54	7.05 ± 0.03	92.99 ± 0.43
50°C - 6 hours - 2M	110.00 ± 2.13	7.45 ± 0.14	98.27 ± 1.90
60°C - 2 hours - 1M	364.00 ± 24.59	2.26 ± 0.15	29.78 ± 1.98
60°C - 2 hours - 1.5M	545.19 ± 11.18	1.50 ± 0.03	19.83 ± 0.41
60°C - 2 hours - 2M	307.75 ± 16.79	2.67 ± 0.14	35.19 ± 1.90
60°C - 4 hours - 1M	215.57 ± 10.07	3.81 ± 0.18	50.21 ± 2.41
60°C - 4 hours - 1.5M	311.49 ± 7.09	2.63 ± 0.06	34.71 ± 0.79
60°C - 4 hours - 2M	288.06 ± 6.99	2.85 ± 0.07	37.53 ± 0.92
60°C - 6 hours - 1M	152.47 ± 5.82	5.38 ± 0.20	70.95 ± 2.66
60°C - 6 hours - 1.5M	145.64 ± 3.68	5.63 ± 0.14	74.24 ± 1.90
60°C - 6 hours - 2M	121.91 ± 13.00	6.77 ± 0.75	89.35 ± 9.88

Table 2: Study of Varied Molar Ratio of Hydrogen Peroxide, Reaction Time, and Reaction Temperature Parameters from ASTM D1652-11 using Formic Acid.

Increasing the reaction time up to 4 hours revealed a variation in the oxirane oxygen content at 50 and 60 °C with increasing molar concentration of hydrogen peroxide up to 2 moles. An excess of hydrogen peroxide at half ratios (i.e. 1.5 moles) revealed lower oxirane oxygen content compared to molar concentrations at 1 and 2 mole ratio. However, higher oxirane oxygen content was obtained at 4 hours compared to 2 hours with increasing molar concentration of hydrogen peroxide. The low oxirane oxygen contents at 2 and 4 hours with increasing molar concentration of hydrogen peroxide and increasing temperature revealed relative conversion to oxirane equal or less than 50 %. The result of the low oxirane oxygen content is due to possible degradation of the epoxide groups. This degradation is a result of hydrolysis (introducing water molecules), the generation of glycerol [12], or regeneration of excess formic acid. The water molecules are introduced due to the formation of performic acid when mixing formic acid and hydrogen peroxide. It is the performic acid that when reacted with the double bonds in the oil leads to the regeneration of excess formic acid that hinders the course of the reaction. Thus, due to hydrolysis, generation of glycerol, and excess formic acid there exist instability of the oxirane rings [13] resulting in the varied oxirane oxygen contents.

Nonetheless, a more stable reaction occurred with increasing the reaction time to 6 hours. This stable reaction resulted in an increase in the oxirane oxygen content as the molar concentration of hydrogen peroxide increased at 50 and 60 °C. The longer the reaction was carried out, the more time was given to break the double bonds in the oil and generate performic acid to create higher epoxide content compared to values at 2 and 4 hours. However, epoxidized soybean oil samples synthesized at 60 °C revealed a decrease in the rate of epoxidation and consequently lower oxirane oxygen content when compared to samples synthesized at 50 °C for 6 hours. This decrease is attributed to degradation of the epoxide rings (oxirane cleavage) due to higher bombardment of the molecules to increase the rate of hydrolysis and possible side reactions. Therefore, the optimum reaction time, reaction temperature and molar ratio of hydrogen peroxide appear to be 6 hours at 50 °C using 2 mole ratio of hydrogen peroxide which yields a 98 % relative conversion to oxirane.

The epoxide equivalent weight was shown to have an inverse relationship with the oxirane oxygen content. This parameter is defined as the weight of resin in grams, which contains 1 g of the equivalent [14] and is important in determining the amount of hardener to use when curing the resin. A higher epoxide equivalent weight indicates lower epoxide groups formed in the resin as revealed by the values indicated in Table 2. Consequently, a higher epoxide equivalent weight indicates less curing agent needed due to less reactivity of the resin which indicates less functional epoxide groups in the resin. Therefore, the amount of curing agent needed for the optimum synthesized soybean oil would be close in weight to the grams of resin being used. For example, 1 gram of resin would require 0.9 grams of maleic anhydride curing agent.

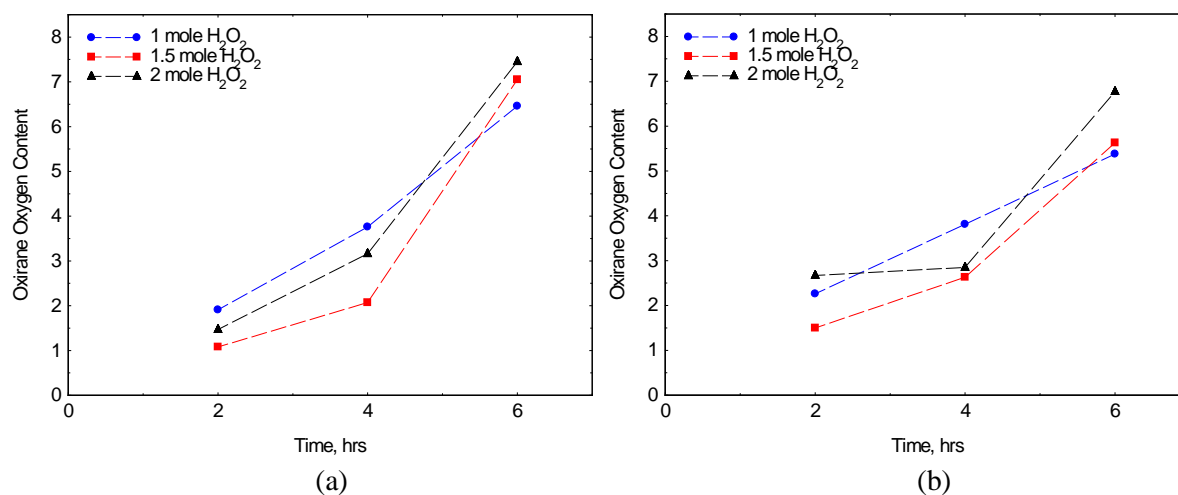


Figure 3: Effect of temperature on oxirane oxygen content at varying time and molar concentration of hydrogen peroxide at (a) 50 °C and (b) 60 °C.

4.2 Fourier Transform Infrared (FTIR) Spectroscopy Studies

Verification into the formation of epoxide groups in ASTM D1652-11 was investigated using FTIR. A characterization peak at 822 cm^{-1} verified the presence of epoxide groups indicating that the double bonds exist and diminishes with increasing reaction time and molar concentration of hydrogen peroxide as indicated by ASTM D1652-11. Figures 4(a) and 4(b) gives a deeper insight into the formation of epoxide groups at 822 cm^{-1} that correlates with data obtained from ASTM D1652-11. Additionally, the result of no epoxide peak gives reasoning for the introduction of side reactions and occurrence of oxirane cleavage that degrades the epoxide rings [7, 15–17]. Other peaks observed from the FTIR spectrum are 3530 cm^{-1} (OH stretching), 3012 cm^{-1} (C-H and C=C stretching) 2920 cm^{-1} (C-H stretching of CH_3), 2850 cm^{-1} (C-H stretching of CH_2), and 1738 cm^{-1} (C=O stretching vibration of carbonyl ester) shown in Table 3. The peak at 3530 cm^{-1} corresponds to the side reactions that disturb the oxirane oxygen content due to OH groups. Verification of this result is expressed by the peak at 3530 cm^{-1} . FTIR peak at 3012 cm^{-1} corresponds to the level of unsaturation that disappears as the double bonds are converted and used [18, 19]; thus, correlating with the epoxide peak at 822 cm^{-1} .

Functional Group	FTIR Wavenumber, cm ⁻¹
OH stretching	3530
C-H stretching	3012
C-H stretching (CH ₃)	2920
C-H stretching (CH ₂)	2850
C=O stretching	1738
C-O-C stretching	1152
C-O-C asymmetric bending	822

Table 3: FTIR wavenumbers revealing the functional groups present in epoxidized soybean oil samples.

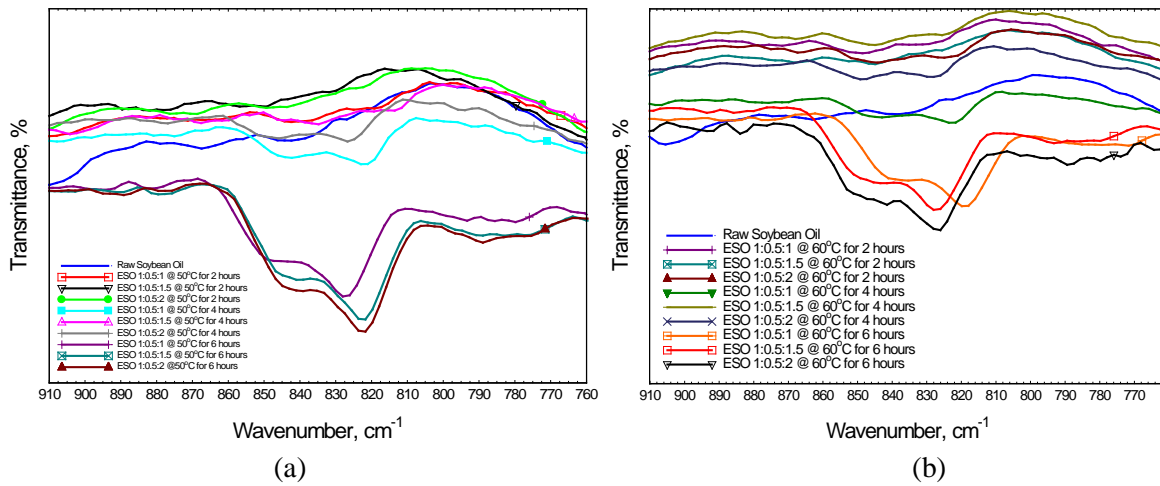


Figure 4: FTIR Spectrum Highlighting the presence of epoxide groups at 822 cm⁻¹ at (a) 50 °C and (b) 60 °C.

4.3 Rheological Studies

The viscosity study of each epoxidized soybean oil system was analyzed to determine processing and performance conditions of each system for composite manufacturing processes. The results for this study are shown in Figures 5(a) and 5(b) for samples synthesized at 50 °C and 60 °C with increasing reaction time and molar concentration of hydrogen peroxide.

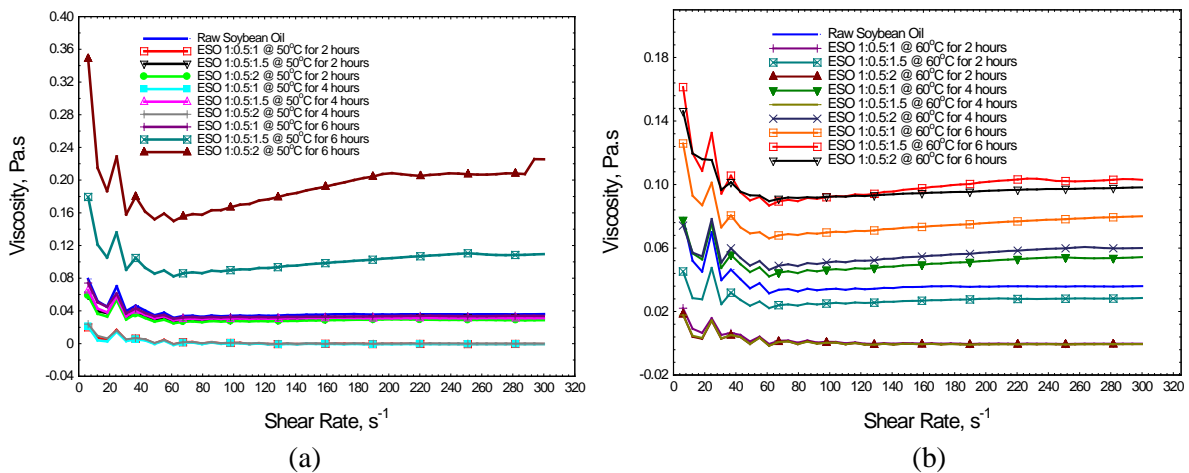


Figure 5: Rheology Plot of Epoxidation Reaction using Formic Acid at (a) 50 °C and (b) 60 °C.

There exists a variation in the viscosity at initial shear rates indicated by the sharp peaks at 28 and 50 s^{-1} . This sharp peak is indicative of bombardment of the molecules as a result of shearing which results in thixotropic behavior. This thixotropic behavior is associated with the molecules in the oils (whether in the raw form or epoxidized form) breaking down and regaining their internal network structure as stress is reduced and removed. At the end of the thixotropic behavior, the oils come to a defined viscosity where Non-Newtonian behavior occurs. The behavior beyond 50 s^{-1} is no longer associated with the molecules, but now reflects either shear thickening, shear thinning, or Newtonian behavior in the manner of the samples flow.

The results in Figures 5(a) and 5(b) reveal lower viscosities for systems that exhibit low oxirane contents and high epoxide equivalent weights suggested by ASTM D1652-11. Samples prepared at 1:0.5:1.5 at 50°C for 4 hours, 1:0.5:1.5 at 60°C for 2 hours, 1:0.5:1 at 60°C for 4 hours, and 1:0.5:2 at 60°C for 4 hours all exhibit shear thickening behavior which relates to structural rearrangement [20]. This shear thickening is reflected mostly for samples with high oxirane contents that exhibit low epoxide equivalent weights. Viscosities lower than that of the raw soybean oil is an indication of the presence of water molecules as a result of hydrolysis, which is more prominent in reactions at lower times.

To ensure complete wetting of fibers used in composite fabrication processes, the viscosity must be low, but not too low that the flow of the resin is great. Typically, resins used in fabrication processes (such as pultrusion, filament winding, resin transfer molding, etc.) has viscosities that range from 0.1 up to 100 Pa.s [21, 22]. Therefore, from Figures 5(a) and 5(b), there is clear indication that only samples synthesized for 6 hours are suitable for use in composite fabrication. In particular, the samples synthesized for 6 hours are more suitable for use in resin transfer molding [23], but includes filament winding [24] for the optimum system synthesized at 50 °C for 6 hours using 2 moles of hydrogen peroxide.

5 CONCLUSIONS AND FUTUREWORK

The effect of time, temperature, and molar concentration of hydrogen peroxide on the compositional and rheological properties was studied for the synthesis of epoxidized soybean oil using FTIR and shear rate Rheometry. Determination into the amount of double bonds converted to epoxide groups (oxirane oxygen content) was found using titration method of ASTM D1652-11. The system was optimized by varying the reaction time at 2, 4, and 6 hours, reaction temperature at 50 and 60 °C, and molar concentration of hydrogen peroxide at 1, 1.5, and 2 mole ratio to yield high conversions of epoxide groups. It was revealed that low oxirane oxygen content was a result of hydrolysis, generation of glycerol, and oxirane cleavage. Overall, epoxidized soybean oil samples synthesized for 6 hours proved to have higher oxirane oxygen contents. Optimum conversion to oxirane was achieved at 6 hours using 2 mole ratio of hydrogen peroxide synthesized at 50 °C. Based on results from ASTM D1652-11, the optimum system yielded an oxirane oxygen content of 7.45 and a percent conversion to epoxide groups of 98%. This result was verified using Fourier transform infrared (FTIR) spectroscopy shown at frequencies of 822 cm^{-1} . Results from rheology also verified results from ASTM D1652-11 showing behaviors of typical epoxy resins of higher viscosities at onset, and shear thinning or shear thickening behaviors as the shear rate increases.

Cure kinetics on the optimized system is future work to determine curing conditions for future use in the fabrication of an advanced green composite. This work is in its initial stages to characterize and synthesis a high bio-based epoxy resin system.

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