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Oxirane Ring Opening of Rubber (Hevea Brasiliensis) Seed Oil by Performic Acid

O.R. Obanla, J.D. Udonne, O.O. Ajani, M.E. Ojewumi O.J. Omodara

Abstract: Studies on the epoxidation of rubber (*Hevea brasiliensis*) seed oil, a renewable source with formic acid was performed in the presence of 30% hydrogen peroxide at a temperature 40, 50,60,70 °C. The process is favoured by an increase in temperature forming a product with high oxirane content which is as a result of mole ratios of formic acid and hydrogen peroxide. Products of high oxirane content are commercially viable in the production of polyvinyl chloride (PVC). Natural rubber and other products can be obtained from this in- situ technique. Studies in this research shows that the rate of epoxidation increases with an increase in temperature. Oxirane values of 2.30, 3.62 and 4.73 for the various temperature. However high oxirane content of 6.22 was obtained at 70 °C which is in line with literature. FTIR analysis was also carried out on the epoxidized rubber seed oil which shows the peaks of oxirane cleavage.

Keywords: Epoxidation, oxirane content, performic acid and rubber seed oil.

I. INTRODUCTION

Sustainable materials are well known to be environmental friendly, inexhaustible, cheap and bountiful [1]. The utilization of these raw materials in various areas has fascinated the responsiveness of many researches due to their potentials as an alternative of petroleum chemical derivatives [2]. The development of this biodegradable material has made it achievable to perform a broad study on the chemical composition and the properties of these vegetable oils [3&4]. In Nigeria, natural oil reliant industries solely rely on importation of oils like castor oil and soybean oil which are quite costly. The readily available oils like coconut oil, groundnut oil and palmkernel oil are in short supply because they are cultivated basically for consumption [5-8].

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O.R. Obanla. Department of Chemical Engineering, Covenant University, Ota, Ogun State, Nigeria. Email: oyinlola.oresegun@covenantuniversity.edu.ng

J.D. Udonne*, Department of Chemical and Polymer Engineering, Lagos State University, Nigeria

O.O. Ajani*, Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria

M.E. Ojewumi*, Department of Chemical Engineering, Covenant University, Ota, Ogun State, Nigeria. Email:

O.J. Omodara*, Department of Chemical Engineering, Covenant University, Ota, Ogun State, Nigeria. Email:

Rubber seed oil has little commercial worth in Nigeria to the best of our realization. Nigeria has the ability of producing over 15,000 tons of rubber seed oil (RSO) annually [9,10]. Earlier research studies have reveals that rubber seed oil is a prospective raw material for binders in surface coatings [9], as printing inks [7&10], biodiesel [9,14-16] processing aid in polymer compounding [11] and manufacture of metallic soaps [12]. The unsaturated fatty acids of this vegetable oils are rich in linolenic and oleic acid. The double bonds present in the fatty acid can be replaced with functional groups like the epoxides [13&15]. Rubber seed oil is used in this case. The desired epoxidized oil can be used as a multifunctional additive for rubber compounding [5&11]. In this study, the synthesis of epoxidized rubber seed oil was carried out by maintaining a particular temperature. The physico chemical properties and spectroscopic data of the product were also established. However, vast work have been reported on the epoxidation of RSO by acetic acid [3,5,6,11] and neither of these reports encompasses the kinetic properties of the finished products. Epoxidation is the reaction of an organic acid with a double bond to form a cyclic three membered ring structure called an epoxide [3&5]. Nevertheless, this paper extends the study of epoxidation of rubber seed oil by substituting acetic acid for formic acid. The organic acid shuttles the active oxygen between the aqueous phase to the oil layer. The research investigates the epoxidization of rubber seed oil by performic acid generated in situ.

II. METHODOLOGY

Crude rubber seed oil (RSO) used in this research was obtained by mechanical expression method. Formic acid (99.5%) obtained from Sigma Aldrich, Poole, England, hydrobromic acid (AR) obtained from Riedel - de Haen and hydrogen peroxide (30%) from MERCK were used without further purification in this study.

A. Preparation of epoxidized rubber seed oil

ERSO was prepared using calculated amount of rubber seed oil, containing 90 % formic acid were placed in a quick fit flask, as shown below in Figure 1a. The flask was continuously stirred and allowed to attain the optimum temperature (controlled to better than ± 2 °C equilibration) and 30 % hydrogen peroxide (80 ml) was added to the oil dropwise with a dropping funnel for over 30 minutes. The stirring rate was maintained at 400 rpm so that oil mixture will be finely dispersed as shown below figure 1b.

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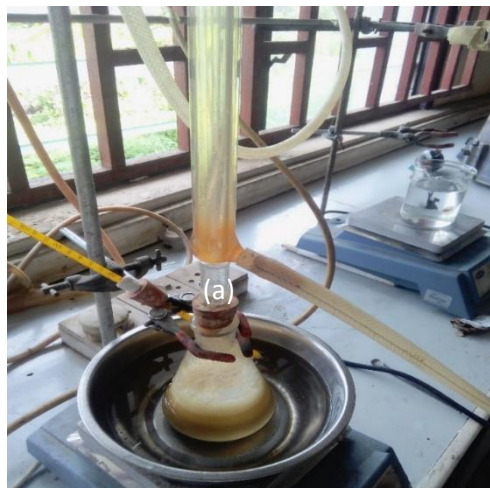


Figure 1a: Equilibration of RSO

Figure 1b: Epoxidation of ERSO Set-up

The reaction temperature was retained at 40 °C, and stirred continuously for 3 hours. The progress of the reaction was examined closely by taking aliquot at different time to measure oxirane content. The experiment was repeated at temperatures of 50, 60,70 °C. The physico- chemical properties and fatty acid profile are given in Table 1 & 2 respectively.

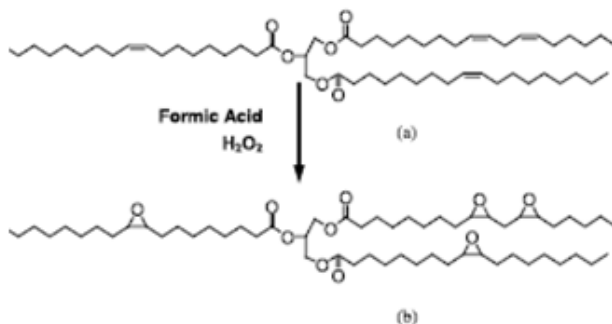


Figure 2: Production pathway of epoxidized rubber seed oil (ERSO)

III. RESULT AND DISCUSSIONS

Table I: The physico- chemical properties of RSO and ERSO at different temperatures

Properties	RSO	ERSO at 40°C	ERSO at 50°C	ERSO at 60°C	ERSO at 70°C
Specific gravity	0.874	0.876	0.874	0.877	0.879

(at 30°C)					
Acid value (mg KOH/g of oil)	173.29	112.58	68.54	34.33	26.42
Saponification value (mg KOH/g of oil)	189.62	303.10	279.14	226.65	217.11
Iodine value (g I ₂ /100g)	134.26	87.32	72.67	42.11	35.30
Oxirane content (%)	-	2.30	3.62	4.73	6.22

Table II: Fatty acid composition of rubber seed oil from GLC

Fatty acids	Percentage (%)
Saturated	
C16:0	Palmitic acid
19.61	
C18:0	Stearic acid
5.73	
Unsaturated	
C18:1	Oleic acid
26.13	
C18:2	Linoleic acid
38.30	
C18:3	Linolenic acid
13.60	

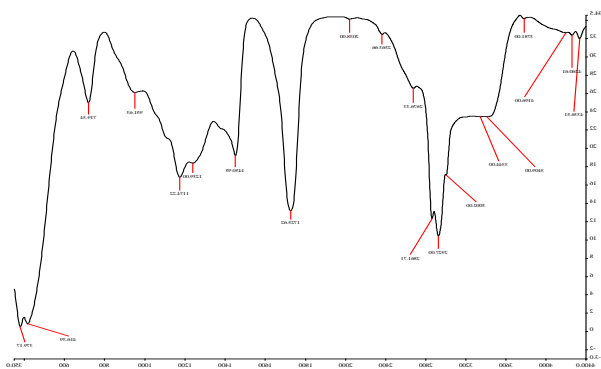


Figure 3: FTIR spectrum of extracted rubber seed oil (RSO)

Table III: Characteristics peak of RSO and their functional groups

Sample	Band (cm ⁻¹)	Assignment
RSO	5781	O-H Overtone
	5002	Combination asymmetric bending of O-H
	4556	Stretching frequency of the of the epoxy ring
	4260	Stretching O-H
	1725-1450	Stretching CH ₃ of (CH ₃) ₂
	1259-1174	bending C-O-C frequency of ethers
	951	bending C-O of oxirane
719	bending C-C of carbon atom	

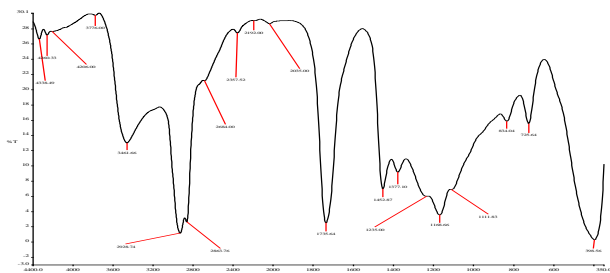


Figure 4: FTIR spectrum of epoxidized rubber seed oil (ERSO)

Table IV: Characteristics peak of ERSO and their functional groups

Sample	Band (cm ⁻¹)	Assignment
ERSO	4338	O-H Overtone
	3461	Combination bending of O-H
	2928	Stretching frequency of the epoxy ring
	2865	O-H stretching
	1255-1377	bending C-H of CH ₂ and CH
	1111-1165	Stretching of ethers
	725	Bending of oxirane group

The FTIR spectrum of RSO showed a bending vibrational mode at 951 cm⁻¹ which depicted the presence of C-H of C=C. This disappears in the FTIR spectrum of ERSO which implies the disappearance of C=C bond. There was an absorption frequency of 1377 cm⁻¹ appearing in the spectrum of ERSO which showed the presence of cyclic ether group of the epoxy functionality. This on the overall, showed that C=C of RSO was effectively and efficiently converted to C-O-C of epoxy functionality.

A. Effect of temperature on epoxidation of rubber seed oil with performic acid

Plots of % oxirane versus time for the epoxidation at different temperatures and time is shown in Figure 4. These plots illustrates that the reaction is rapid at a higher temperature. At 40 °C, the reaction rate increases somehow slowly with time. However, at temperature of 50 °C and above are linear at the beginning of the reaction (up to about 3 hours of the reaction) when an upward curvature is obtained. This upward curvature is believed to mark the beginning of the oxirane ring opening reaction that could lead to a decrease in the epoxide content of the reaction mixture. It has been reported by [3] that the time attaining these maximum epoxide content decreases as the temperature increases and are much shorter for epoxidation with performic acid thereby making epoxidation of RSO with performic acid more economical. These results therefore propose that favourable level of epoxidation could be achieved at mild temperatures of (60 -70 °C) at which epoxide appears to be minimal.

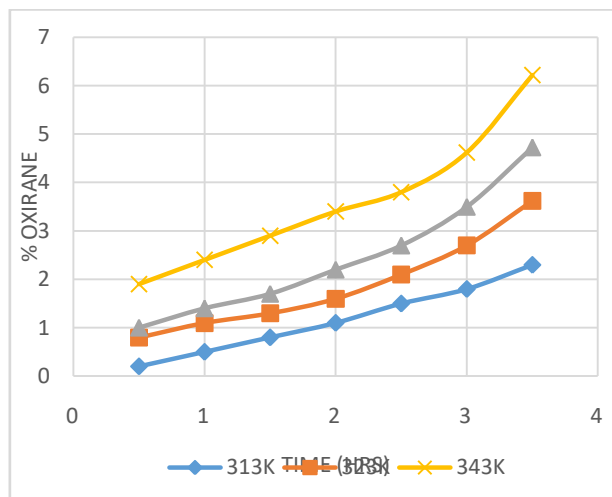


Figure 5: Plots of % oxirane content versus time at different temperatures.

B. Kinetics analysis of epoxidation

The rate expression for the epoxidation was reported by [5]

$$\ln\{[H_2O_2] - [EP]\} = k[RCOOH]_0 t + \ln [H_2O_2] \quad (1)$$

where

EP represents the epoxides and subscript denotes the initial concentration.

$[H_2O_2]_0$ and $[HCOOH]_0$ are the initial concentrations of hydrogen peroxide and formic acid respectively. K is the rate constant while t is the time of reaction. From equation 1 plots of $\ln\{[H_2O_2] - [EP]\}$ versus t is assumed to be linear from which the K for epoxidation can be obtained. Figure 6 illustrates the plots of $\ln\{[H_2O_2] - [EP]\}$ versus t different temperatures. The nonconformities of linearity suggests to be as a result of oxirane degradation. The values of the K were obtained from the initial linear plots and are given in Table 5. These high K values for the epoxidation with performic acid can be attributed to the stronger acidic nature and the active oxygen nature of formic acid which makes it more efficient and effective than acetic acid in shuttling the active oxygen site between the aqueous phase and oil phase which is centered on epoxidation.

Table V: Value of K, calculated for the epoxidation of RSO by performic acid obtained at different temperatures

Temperature of reaction (K)	Rate constant Performic acid $k \times 10^5$ (L mol ⁻¹ s ⁻¹)
313	1.61
323	6.43
333	9.32
343	17.64

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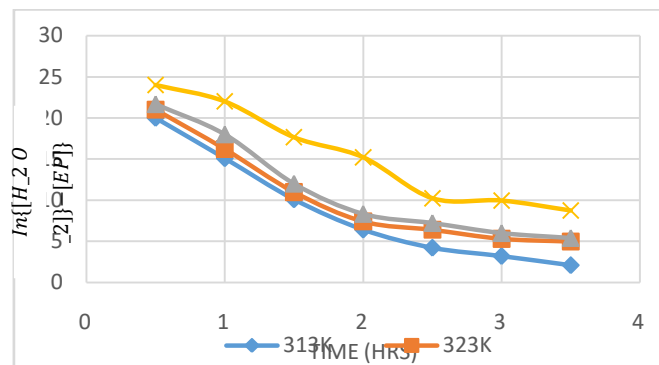


Figure 6: Plots of $\ln\{[H_2O_2]\} - [EP]$ versus reaction time at different temperatures

The activation energy (E_a) and the enthalpy of reaction (ΔH) of epoxidation of RSO with performic acid are 67KJmol^{-1} and 62.4KJmol^{-1} . These values are lower than $E_a = 74\text{KJmol}^{-1}$ and $\Delta H = 68\text{KJmol}^{-1}$ as reported earlier for epoxidation of RSO with peracetic acid [5]. These thermodynamic parameters tend to indicate that it is energetically feasible and viable to epoxidize rubber seed oil with performic acid than with peracetic acid.

IV. CONCLUSION

From the results obtained from this study, it can be inferred that epoxidized rubber seed oil with high epoxide content is favoured by a high temperature, but epoxidation is accompanied by oxirane cleavage which makes it suitable in production of plasticizers. Highest epoxide content of 6.22 is achieved at high temperature of 343K. However, from the kinetic and thermodynamic values obtained for epoxidation, it simply indicates that an increase in the reaction temperature leads rapid epoxide formation and this is very beneficial for scaling up making of epoxidized oils employing *in situ* method.

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ETHICS

This paper has neither been published nor submitted in any domestic or abroad journals.

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AUTHORS PROFILE



Oyinlola Obanla holds a 1st and 2nd degree in chemical Engineering. A versatile Researchers that specializes in Polymer Engineering



Prof. Joseph Udonne is a chemical Engineer who specializes in recovery resources and Polymer Technology.



Prof. Olayinka Ajani is a researcher with area of specialization in organic synthesis and medicinal chemistry