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Epoxidation of Novel Wild Jack Fruit Seed Oil: Effect of Temperature

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Bio-based epoxy system have acquired scientific attention due to their renewability, easy availability, low cost, bio degradability and reduced toxicity. Vegetable seed oils are promising source for the preparation of bio-epoxy networks. In the present work, oil was extracted from wild jack fruit (Artocarpus Hirsutus) seeds using petroleum ether and was found to be ~19 %. The fatty acid composition of wild jack fruit seed oil (WJO) analyzed using gas chromatography revealed an unsaturation content of ~42 % which was further confirmed by iodine value. The extracted WJO was epoxidized with insitu formed peroxy-acetic acid at three different temperatures viz. 45 oC,60 oC and 75 oC using sulphuric acid as the catalyst resulting in epoxidized wild jackfruit seed oil (EWJO). The titrimetric determination of iodine value and oxirane value and the spectroscopic investigation using proton NMR suggests 60 oC as the optimum temperature for the epoxidation of wild jackfruit seed oil.
Keywords: Epoxidation; Artocarpus Hirsutus; proton NMR; seed oil.

1. Introduction

Epoxy resins are widely used thermosetting polymers with remarkable properties such as high mechanical strength, excellent chemical resistance and dimensional stability and hence extensively used in applications such as structural materials, paints, coatings, electrical encapsulation, composites etc. [1]. The conventional epoxy resin DGEBA (Diglycidyl Ether of Bisphenol A) makes use bisphenol A and epichlorohydrin as monomers that are of petroleum origin. Many detrimental effects to human health have been reported by the usage of bisphenol-A in the production of DGEBA. The toxic effects of bisphenol A associated with high cost and depletion of petroleum resources urge the industries to find suitable alternatives to replace at least partially, the petroleum derived resins [2]. So, there is an increasing demand for sustainable materials that are safe to our environment. Plant-based materials such as rosin, lignin, itaconic acid and vegetable oils belong to such a class of promising materials [3].

Vegetable oils are triglycerides of saturated as well as unsaturated fatty acids. The advantage of unsaturated sites in vegetable oils is that they can be functionalized via reactions such as epoxidation, transesterification and hydroxylation etc. The epoxidation reaction can convert the double bonds present in oils into reactive epoxy ring [4,5]. The major unsaturated fatty acids present in oils are oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3). The percentage of fatty acids in a particular oil also can vary depending on the condition in which the plant growth takes place. A high extent of unsaturation in an oil facilitates the formation of epoxidized oils which can be potential alternative for the commercial epoxy resin [6]. In a conventional epoxidation reaction, an oxygen donor such as hydrogen peroxide reacts with carboxylic acids such as acetic acid to form in-situ peroxyacetic acid. The peroxy acid formed oxidizes the double bonds to three-membered epoxy ring systems. Inorganic acids such as sulphuric acid and nitric acid are used as catalysts in the conventional epoxidation method [7,8]. Parameters such as temperature, reaction time, amount and type of catalyst used, ratio of unsaturation to H_2O_2 and ratio of unsaturation to CH_3COOH can influence the extent of epoxidation and these conditions have to be optimized for a particular oil.

The different vegetable oils that have been used for epoxidation includes perilla seed oil, castor oil, linseed oil, hemp oil etc. [2-6]. However, the widespread application of epoxy demands for novel oils with higher content of unsaturated fatty acids. Moreover, a great deal of attention is given to non-food-based oils so as to evade the threat to the availability of oils in the food sector [5].

Wild jackfruit is found in the evergreen forests of Western Ghats, India. Its fruits are bright yellow, sweet, edible and the seeds contain nearly16-17 % of oil. The seed oil has medicinal value and is used in the treatment of asthma and skin diseases [9]. The tree is mostly appreciated for its durable timber, however, the seeds as well as the fruit remains under-utilized in most of the places. The industrial value of wild jack fruit seed oil is yet to be explored and the present work focuses on the preparation and characterization of epoxidized wild jackfruit seed oil, a bio-based epoxy prepolymer system. The study also includes the optimization of reaction temperature under the conditions in which reaction was performed.

2. Experimental Section

Materials

The wild jack fruit seeds were collected from Ernakulam district of Kerala, India. All the chemicals used for the study were supplied by Merck Life Science Pvt. Ltd., Mumbai, India and were used as received.

Extraction of WJO

The wild jack fruit seeds were collected, washed, dried, powdered and the seed oil was extracted using petroleum ether for 6 h and the oil was separated from the solvent with the help of a rotavapor.

Epoxidation of WJO

The extracted WJO was taken in a three neck RB flask and calculated amount of acetic acid and sulphuric acid (2% of volume of CH_3COOH and H_2O_2) were introduced into the flask. It

was stirred for 30 minutes and then, calculated amount of H_2O_2 was added dropwise into the reaction medium. When the addition of H_2O_2 was complete, the reaction was continued for 6 hours. The double bond in oil: CH_3COOH: H_2O_2 ratio was maintained as 1:0.5: 1.5 [10]. After the reaction, the epoxidized oil (EWJO) was separated, washed free of acid and dried using anhydrous sodium sulphate. In order to study the effect of temperature on extent of epoxidation, the reaction was carried out at three different temperatures viz. 45 ^oC, 60^o C and 70 ^oC and the samples were represented as EWJO45, EWJO60 and EWJO75 respectively.

Characterization

The fatty acid composition of the oil was analyzed using a 6890N gas chromatograph combined with 5975 MSD. The iodine value was determined using Wijs solution as per ASTM D5768. Oxirane value was determined using HBr-acetic acid according to ASTM D 1652. The proton NMR analysis was done using JEOL(JNM-ECZ400S) NMR spectrophotometer at a frequency of 400 MHz using deuterated chloroform as the solvent.

3. Results and Discussion

Fatty acid composition

The different stages of extraction of wild jackfruit seed oil are shown in Fig.1.

Fig 1. Extraction stages of WJO

The yield of WJSO from the dried seeds was found to be 18.7 %. The fatty acid composition of WJO is given in Table1 which shows approximately 42 % unsaturated fatty acids present in the oil and the major one being linoleic acid containing two double bonds in the chain.

Table 1: Fatty acid composition of wild jack fruit seed oil

Fatty acid	Percentage
Linoleic acid (C18 :2)	36.7
Lignoceric acid (C24:0)	27.6
Palmitic acid (C16:0)	13.5
Oleic acid (C18: 1)	4.1
Cis-11-Eicosenic acid (C20: 1)	1.1

Iodine value

Iodine value is the measure of average double bonds present in an oil and is defined as the grams of iodine required to react with 100 g of oil [11]. The iodine value (I.V.) can be calculated using the Eq.1

$$\text{I.V.} = \frac{(\text{B}-\text{T})\ \text{x}\ \text{N}\ \text{x}\ 12.69}{\text{W}} \quad (1)$$

where N is the normality of sodium thiosulphate; B and T, the volume of thiosulphate (ml) for blank and sample titration, respectively and W represents the weight (g) of oil [12].

The iodine value of oil as well as epoxidized oils can be used to determine the double bond conversion (DBC) happening via epoxidation reaction by Eq. (2)

$$\text{DBC}\ \ (\%)\ = \frac{\text{I.V.}_\text{f}-\text{I.V.}_\text{i}}{\text{I.V.}_\text{i}}\ \times\ 100 \quad (2)$$

where I.V._i represent iodine value of oil and I.V._f represents iodine value of epoxidized oil.

The iodine value of WJO was found to be 106.8 g/100 g oil. For the epoxidized oils, it is found that, with increase in temperature, the iodine value decreases considerably and for the 75 ^{o}C sample, no value is observed for the same. The values obtained are in the order EWJO45 (48.2) > EWJO60 (35.9) > EWJO75 (0). The substantial decrease in I.V. with increase in temperature can be due to the enhanced activation attained for the insitu formation of peroxy acetic acid, which causes the epoxidation reaction. The DBC achieved by the epoxidation reaction at different temperatures is shown in Fig. 2. Since the I.V. decreases with increase in temperature, the DBC increases correspondingly and it is seen that at 75 ^{o}C, no iodine value is observed which means no double bonds are present in EWJO75 and it shows100% DBC [13].

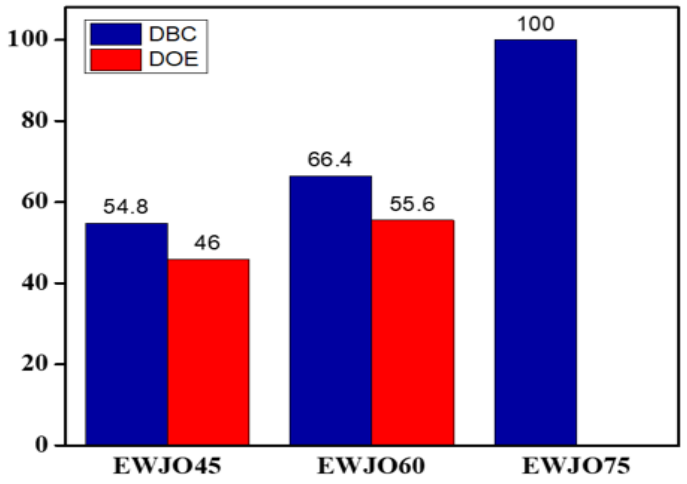

Fig.2. DBC and DOE estimated using titrimetric method

Oxirane value

Oxirane value (OO_e) is a measure of the 'g' of oxirane oxygen present per 100 g of oil sample.

The theoretical oxirane oxygen value (OO_t), experimental oxirane oxygen value (OO_e), and degree of epoxidation (DOE) were calculated using Eq. (3), (4), and (5) respectively [1,14].

$$OO_t = \left(\frac{\frac{IV_O}{2A_I}}{100+\left(\frac{IV_O}{2A_I}\right)A_O} \right) A_O \times 100 \quad (3)$$

where A_I and A_O represent the atomic masses of iodine and oxygen, respectively.

$$OO_e = \frac{V \times N \times 1.6}{W} \quad (4)$$

where V and N represents the volume and normality of HBr-acetic acid solution and W is the weight of the epoxidized oil.

$$DOE = \frac{OO_e}{OO_t} \times 100 \quad (5)$$

The theoretical oxirane value of WJSO, calculated based on its iodine value was found to be 6.3 g/100 g oil. The experimentally determined oxirane value for EWJO45 was 2.9g/100 g and that for EWJO60 was 3.5 g/100 g. However, for EWJO75, the oxirane value was found to be zero. This indicates that an increase in temperature from 45 ^oC to 60 ^oC caused an increase in oxirane value reflecting greater epoxidation, but a further increase in temperature to 75 ^oC caused a decline in oxirane value to zero indicating the absence of epoxy groups in the system. But for EWJO75 system, the iodine value shows100% of double bond conversion and so it can be concluded that even though all the double bonds have been converted to epoxy, due to high activation achieved by high temperature, all the epoxy groups might have undergone ring opening resulting in a DOE value of zero. The DOE achieved for the T45 and T60 reaction systems is shown in Fig.2 and maximum DOE is achieved for the EWJO60 sample. So, an increase in reaction temperature can enhance the reaction rate by providing sufficient activation energy, but the possibility of ring opening side reactions must be considered which becomes prominent at higher temperatures. Based on these results, it is found that the optimum temperature for the epoxidation of WJO is 60 ^oC.

Proton NMR Spectrum

The ^{1}H-NMR spectra signals of WJO and EWJO at different temperatures are illustrated in Fig.3. For WJO, the multiplet signal at 5.2-5.5 ppm is indicative of the vinyl protons attached to the double bonds. After the epoxidation reaction, the intensity of vinyl hydrogen signal at 5.2-5.5 ppm reduces considerably due to the formation of epoxide group [15,16]. Also, the presence of new peak in EWJO at 2.9-3.2 ppm confirms the formation of epoxy rings on the unsaturated sites of WJO leading to the formation of EWJO. The NMR spectrum of EWJO75 shows peaks neither in the 5.2-5.5 ppm range nor in 2.9-3.2 ppm range reflecting the absence of both double bonds and epoxy group.

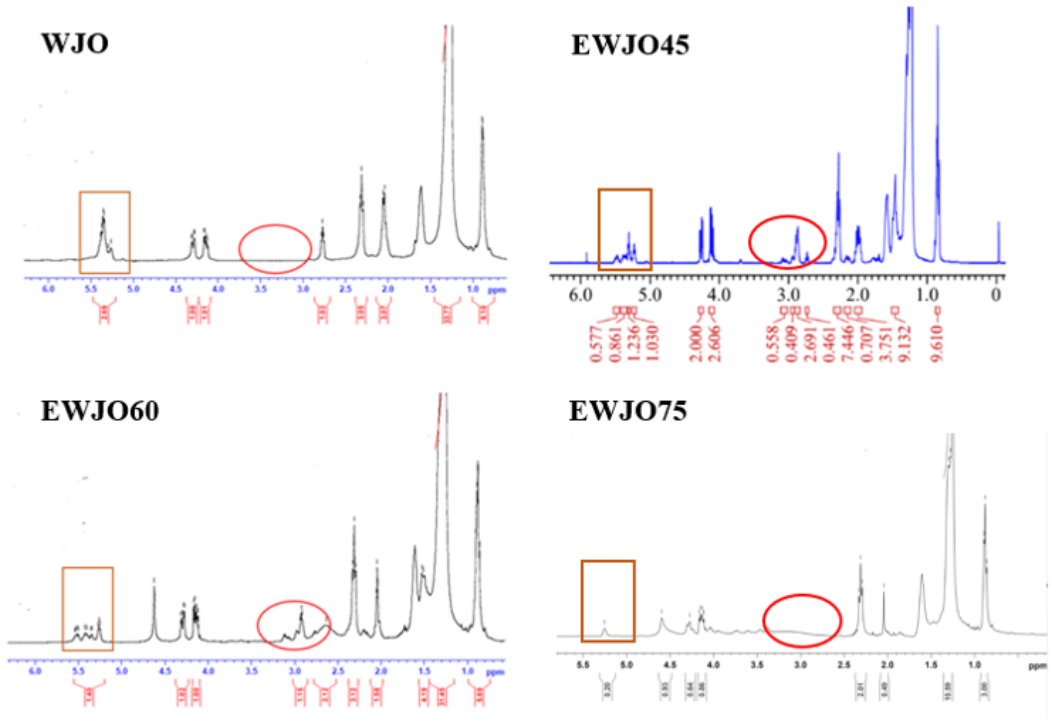

Fig.3 Proton NMR Spectra of WJO and EWJO

^{1}H NMR is an excellent tool for quantitative estimation of the unsaturation present in the oil and the degree of epoxidation happened in epoxidized systems. From the peak areas of the recorded NMR spectrum, the number of double bonds present in WJO (ND_i) was determined using Eq. (6)

$$ND_i = \frac{A-NF}{2NF} \quad (6)$$

where A is the peak area of olefinic hydrogen (5.2-5.5 ppm) and normalization factor (NF) can be calculated by Eq. (7)

$$NF = \frac{B}{4} \quad (7)$$

where B is the peak area assigned to the four methylene hydrogens of glycerol moiety (4.1-4.2 ppm)

The double bond conversion (DBC) %, degree of epoxidation (DOE) % and selectivity % are estimated using Eq. (8), (9) and (10), respectively [5,17] and the results are shown in Fig.4.

$$DBC\ (\%) = \left[\frac{ND_i - ND_f}{ND_i}\right] \times 100 \quad (8)$$

$$DOE\ (\%) = \left[\frac{\left(\frac{I+J}{2}\right)}{NF.ND_i}\right] \times 100 \quad (9)$$

where I and J are peak areas attributed to the hydrogen of epoxy ring (2.9-3.2 ppm) and ND_f is the number of double bonds that remain unreacted after epoxidation and can be determined using Eq. (6) by substituting appropriate peak areas of the spectrum of epoxidized sample.

$$\text{Selectivity (\%)} = \frac{\text{DOE \%}}{\text{DBC \%}} \times 100 \tag{10}$$

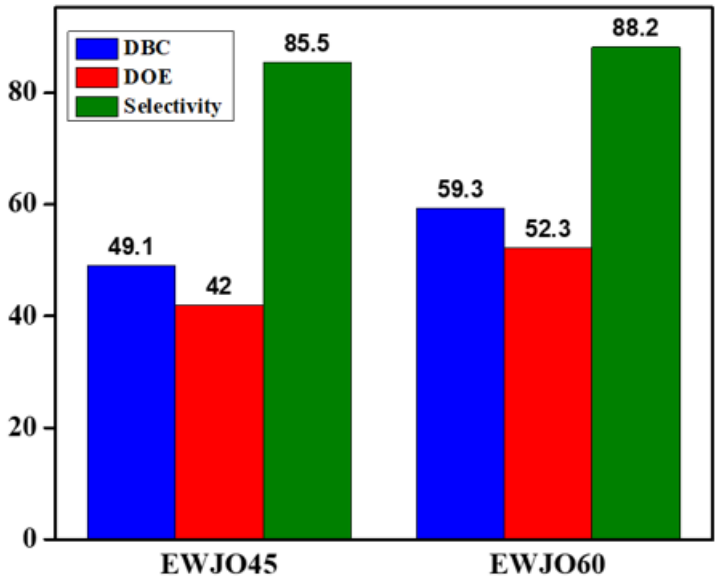

Fig. 4 DBC, DOE and selectivity based on NMR studies

In the case of EWJO45, the DBC and DOE values calculated using NMR spectrum indicates that out of the 49.1% DBC, 42% is converted into epoxy with a selectivity of 85.5%. For EWJO60, the DBC values improved to 59.3% and 52.3% oxirane conversion was achieved with an improved selectivity of 88.2% indicating lesser epoxy ring opening side reactions. So, epoxidation is better at a temperature of 60 ºC. The results obtained for the 75 ºC system (EWJO75) indicates the prominence of epoxy ring opening side reactions with increase in temperature [18]. Here in EWJO75 the peak area in the range 5.2-5.5 ppm is negligible corroborating ~100 % conversion of double bonds, at the same time no peaks are observed for epoxy group also. The iodine value and oxirane value measurements also supports this finding. So, the quantitative spectroscopic analysis by proton NMR suggests the optimum temperature for epoxidation of WJO as 60 ºC under the conditions in which reaction was performed.

4. Conclusion

WJO was extracted from the seed powder using petroleum ether as the solvent with a yield value of 18.7%. Using the extracted oil, epoxidation was carried out at three different temperatures 45,60 and 75 ºC using insitu formed peroxy acetic acid and sulphuric acid catalyst. The iodine value and oxirane value determination revealed maximum epoxidation (55.6%) for the EWJO60 system. Spectroscopic analysis also showed maximum value of

52.3% epoxidation for EWJO60 and it can be concluded that optimum temperature for epoxidation is 60 ºC under the selected reaction conditions. Hence, wild jack fruit seed can be considered as a green source for the extraction of seed oil and the oil can be a potential material for the synthesis of a sustainable, non-toxic epoxy pre polymer system. Further studies have to be conducted for the optimization of other reaction parameters such as reaction time, catalyst and reagent ratio etc. for the epoxidation of WJO in order to achieve a higher degree of epoxidation.

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References

1. Latif, F. E. A., Abidin, Z. Z., Cardona, F. R. A. N. C. I. S. C. O., Biak, D. A., Tahir, P. M., Abdan, K. H. A. L. I. N. A., & Liew, K. (2019). Physicochemical, structural and mechanical evaluation of bio-based epoxidized jatropha oil blended with amine-cured epoxy resin as new hybrid matrix. Journal of Engineering Science and Technology, 14(2), 1071-1087.
2. Kousaalya, A. B., Beyene, S. D., Gopal, V., Ayalew, B., & Pilla, S. (2018). Green epoxy synthesized from Perilla frutescens: A study on epoxidation and oxirane cleavage kinetics of high-linolenic oil. Industrial Crops and Products, 123, 25-34. https://doi.org/10.1016/j.indcrop.2018.06.047
3. Sudha, G. S., Kalita, H., Mohanty, S., & Nayak, S. K. (2017). Biobased epoxy blends from epoxidized castor oil: Effect on mechanical, thermal, and morphological properties.Macromolecular Research, 25, 420-430. DOI 10.1007/s13233-017-5063-3
4. Sahoo, S. K., Khandelwal, V., & Manik, G. (2018). Development of toughened bio-based epoxy with epoxidized linseed oil as reactive diluent and cured with bio-renewable crosslinker. Polymers for Advanced Technologies, 29(1), 565-574. https://doi.org/10.1002/pat.4166
5. Wai, P. T., Jiang, P., Shen, Y., Zhang, P., Gu, Q., & Leng, Y. (2019). Catalytic developments in the epoxidation of vegetable oils and the analysis methods of epoxidized products. RSC advances, 9(65), 38119-38136. https://doi.org/10.1039/C9RA05943A
6. Omonov, T. S., Patel, V., & Curtis, J. M. (2019). The development of epoxidized hemp oil prepolymers for the preparation of thermoset networks. Journal of the American Oil Chemists' Society, 96(12), 1389-1403. https://doi.org/10.1002/aocs.12290
7. Dominguez-Candela, I., Lerma-Canto, A., Cardona, S. C., Lora, J., & Fombuena, V. (2022). Physicochemical characterization of novel Epoxidized vegetable oil from chia seed oil. Materials, 15(9), 3250. https://doi.org/10.3390/ma15093250
8. Janković, M. R., Govedarica, O. M., & Sinadinović-Fišer, S. V. (2020). The epoxidation of linseed oil with in situ formed peracetic acid: A model with included influence of the oil fatty acid composition. Industrial Crops and Products, 143, 111881. https://doi.org/10.1016/j.indcrop.2019.111881
9. Krishnapriya, K., & Kanjana, K. (2019). Proximal and Phytochemical Analysis of Wild Jack Fruit Seeds (Artocarpus hirsutus Lam.), Anti-Diabetic and Anti-Microbial Properties and Formulation of Food Products. Journal of Research in Siddha Medicine, 2(2), 88-93.
10. Varghese, T. P., & Gopalakrishnan, J. (2023). Effect of peroxide concentration on the epoxidation of vegetable seed oil. Materials Today: Proceedings. https://doi.org/10.1016/j.matpr.2023.11.069

11. Alarcon, R. T., Gaglieri, C., Lamb, K. J., North, M., & Bannach, G. (2020). Spectroscopic characterization and thermal behavior of baru nut and macaw palm vegetable oils and their epoxidized derivatives. Industrial Crops and Products, 154, 112585. https://doi.org/10.1016/j.indcrop.2020.112585
12. Koley, R., Kasilingam, R., Sahoo, S., Chattopadhyay, S., & Bhowmick, A. K. (2021). Synthesis and characterization of epoxidized neem oil: A bio-derived natural processing aid for elastomer. Journal of Applied Polymer Science, 138(20), 50440. https://doi.org/10.1002/app.50440
13. Ashine, F., Balakrishnan, S., Kiflie, Z., & Tizazu, B. Z. (2023). Epoxidation of Argemone mexicana oil with peroxyacetic acid formed in-situ using sulfated tin (IV) oxide catalyst: Characterization; kinetic and thermodynamic analysis. Heliyon, 9(1). https://doi.org/10.1016/j.heliyon.2023.e12817
14. Suzuki, A. H., Botelho, B. G., Oliveira, L. S., & Franca, A. S. (2018). Sustainable synthesis of epoxidized waste cooking oil and its application as a plasticizer for polyvinyl chloride films. European Polymer Journal, 99, 142-149.
15. Cogliano, T., Turco, R., Russo, V., Di Serio, M., & Tesser, R. (2022). 1H NMR-based analytical method: A valid and rapid tool for the epoxidation processes. Industrial Crops and Products, 186, 115258. https://doi.org/10.1016/j.indcrop.2022.115258
16. Xia, W., Budge, S. M., & Lumsden, M. D. (2016). 1 H-NMR characterization of epoxides derived from polyunsaturated fatty acids. Journal of the American Oil Chemists' Society, 93, 467-478. https://doi.org/10.1007/s11746-016-2800-2
17. Farias, M., Martinelli, M., & Bottega, D. P. (2010). Epoxidation of soybean oil using a homogeneous catalytic system based on a molybdenum (VI) complex. Applied Catalysis A: General, 384(1-2), 213-219. https://doi.org/10.1016/j.apcata.2010.06.038
18. Kim, N., Li, Y., & Sun, X. S. (2015). Epoxidation of Camelina sativa oil and peel adhesion properties. Industrial Crops and Products, 64, 1-8. https://doi.org/10.1016/j.indcrop.2014.10.025