

Production of bio-epoxide and bio-adhesive from non-edible oil

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Abstract—Epoxidation of Nahor oil was performed by H_2O_2 in the presence of acid catalyst at 50 °C. It was possible to obtain around 70% epoxide yield within 8 hrs of reaction. Amberlite IR 120H showed better epoxide yield compared to H_2SO_4 and Dowex 50 WX8. The performance of carboxylic acids was found to be in the order of formic acid > acetic acid > propanoic acid. The curing of epoxidized nahor oil involved using ethylenediamine (EDA) and diethylenetriamine (DETA). The adhesive property of the cured resins was tested and compared with commercially available glue. The force required to detach the cardboard joint was about 36.3 N for DETA-cured resin.

Keywords: Nahor Oil, Carboxylic Acid, Acid Catalyst, Epoxy Resin, Amine Curing, Adhesive

INTRODUCTION

Sustainable development has become the focus of research in every corner of the world. It includes the development of environmentally friendly processes and products. “Renewable resource” is becoming a buzzphrase because of depleting of environmental concerns and depleting of oil reserves. In search of renewable resources for day-to-day products, people are looking at valuable alternatives from natural sources [1,2]. Products obtained from plant oil are known to be environment friendly, cleaner, and mostly biodegradable. Vegetable oils have some specific properties that are required for lubricant applications. Conversion of unsaturated $-C=C-$ double bond into epoxide ring via epoxidation process has received special attention for synthesizing bio-lubricant stock, which can be further cured with a suitable curing agent to make adhesives [3]. Epoxidation of plant oils is a commercially important reaction, because the epoxides obtained from these renewable raw materials have a wide range of applications, such as making plasticizers and polymer stabilizers. Due to the increasing demand for petroleum-based epoxy resin, the epoxidized vegetable oil came into existence with its tremendous applications in the field of paints and coatings, besides acting as a good stabilizing agent [4].

Epoxides are stable intermediates that can be converted to various products like glycols, carbonyl compounds, polyesters, polyurethanes, etc. [5]. Epoxidation depends on many parameters, such as type of feedstock, catalyst used, and temperature. Okieimen et al. studied the epoxidation of rubber seed oil by peroxyacetic acid generated in-situ, from acetic acid and hydrogen peroxide [6,7]. The literature shows that around 50% epoxide yield was obtained after 8.5 hrs at 50 °C. Rangarajan et al. studied kinetics of in-situ epoxidation of soybean oil by peracetic acid in the presence of acid catalyst [8,9]. Epoxidized soybean oil is produced at a large scale for synthesis of plasticizers and polymer stabilizers [10,11]. Dinda et

al. studied the kinetics of epoxidation of cottonseed oil by peroxyacetic acid in the presence of H_2SO_4 and acidic ion exchange resin Amberlite IR 120H as acid catalyst [12,13]. The study shows that selectivity of epoxide product is better in the presence of Amberlite IR 120H compared to H_2SO_4 under similar conditions. Goud et al. studied the epoxidation reaction of karanja and jatropha oil by hydrogen peroxide and acetic acid catalyzed by Amberlite IR 120H [14,15]. The study shows that around 72% epoxide conversion is possible after 6 hrs of reaction at 60 °C.

Major ingredients of an epoxy adhesive are an epoxide material and a hardener/curing agent. Amines are widely used as curing agents for epoxide materials. Curing amine may be primary, secondary, or tertiary. It is known that the curing time and strength of cured product highly depends on the nature of amine used for curing. The more active hydrogen that is present in an amine, the curing will be faster and product will be stronger. Garcia et al. and Liu et al. studied the adhesive strength of glued epoxy resins on metals. The article shows that an amine-cured epoxy material can produce an adhesive strength in the range of 10-15 MPa [16,17]. The strength of adhesive bonding depends on mechanical properties of adherend-adhesive interface. Katnam et al. studied the influence of adhesive thickness on bond strength [18].

The cost of a bio-based epoxide or epoxide derivative depends highly on availability and cost of raw material. Various types of edible and non-edible plant oils, namely cottonseed, groundnut, sunflower, karanja, and nahor oil, are very common in tropical countries. Epoxidation of edible oils may not be cost effective and not a better solution to agro-economic growth. Hence, it would be always better to target large number of non-edible plant oils to study the epoxidation reactions. The progress on the utilization of various oils, such as, karanja, jatropha, rubber seed, cottonseed etc. for epoxide synthesis at laboratory level, is very encouraging towards development of an efficient epoxidation process. Based on the literature survey, no article was found on epoxidation of Nahor oil. Nahor trees are very common in tropical countries like India, Sri Lanka, Nepal, Burma, Thailand, Indochina, Philippines, Malaysia and Sumatra, where they grow in evergreen forests, especially in river valleys.

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Nahor seed kernel contains about 70 wt% oil with an unpleasant pungent odor and it is not used as edible oil [19]. Nahor oil, with a fatty acid composition of around 54% oleic acid ($C_{18:1}$) and 19% linoleic acid ($C_{18:2}$), is an appropriate raw material for epoxidation reaction. Epoxidized nahor oil can be a promising raw material for making bio-lubricant or as an intermediate feedstock for chemical industries.

The present study can be divided into two objectives. The first is preparation of an epoxide material from nahor oil (*Mesuaferrea Linn*), and the second objective is curing of epoxidized oil to develop an epoxy-based adhesive. Epoxidation of nahor oil was carried out using different carboxylic acids, in the presence of different acid catalysts to obtain an optimum epoxide yield. Two different amine compounds were used for curing of epoxidized nahor oil. The present study also includes the characterization and testing of various physico-chemical properties of the epoxidized oil and cured products (adhesive).

EXPERIMENTAL DETAILS

1. Materials

Nahor oil (*Mesuaferrea Linn*) was obtained from Sanjeevani Herbal Health Society, Hyderabad, India. Chemicals, such as glacial acetic acid (CH_3COOH), formic acid ($HCOOH$), propanoic acid (CH_3CH_2COOH), 50% aqueous hydrogen peroxide (H_2O_2), Amberlite IR 120H, Ethylenediamine (EDA), Diethylenetriamine (DETA), and Sulfuric acid (H_2SO_4) used for epoxidation reaction and curing of epoxide were purchased from S D Fine-chem Ltd. (Mumbai, India). Dowex 50 WX8 was obtained from Sigma Aldrich. All other chemicals, such as sodium thiosulphate ($Na_2S_2O_3$), hydrogen bromide (HBr), iodine trichloride (ICl_3), iodine, chlorobenzene, potassium iodide, diethyl ether for analytical purpose were from S D Fine-chem Ltd. (Mumbai, India).

2. Experimental Setup and Epoxidation Procedure

Epoxidation reactions were carried out in a glass reactor equipped with a four-bladed turbine type stirrer. The reactor setup was fixed in a thermostatic water bath to maintain a constant ($\pm 1^\circ C$) reaction temperature. About 100 g nahor oil, calculated amount of organic carboxylic acid and acid catalyst were taken into the reactor, and the mixture was stirred at 1,600 rev/min for about 20 min at $30^\circ C$. Thereafter, the required amount of aqueous H_2O_2 was added drop-wise to the reaction mixture over a period of 30 min. The reaction was continued for more than 10 hrs at a desired temperature. The extent of epoxidation reaction was monitored by withdrawing samples at regular intervals and analyzing its iodine value, oxirane value, and glycol content.

After completion of epoxidation reaction, the epoxidized nahor oil (ENO) was washed with warm water and then extracted with diethyl ether to enhance the separation of the oil product from aqueous phase. A trace quantity of water was removed by using a rotary centrifuge. To study the curing property of ENO, a fixed amount of ENO was taken in two separate beakers and the required amount of amine was added under stirring environment. The amount of amine was calculated based on the molar ratio of the oxirane oxygen and the number of active hydrogens present in the amine. Curing reaction was performed at around $80^\circ C$ using a hot plate

magnetic stirrer. The cured resin obtained was highly viscous and sticky. Various analysis, such as, viscosity, NMR, and tensile test, were performed to characterize the cured products.

3. Chemical Analysis

Iodine value was determined according to Wijs method [20]. The following expression was used to calculate the iodine value.

$$\text{Iodine value (g I}_2\text{/100 g oil)} = \frac{12.69 \times (V_B - V_S) \times N_{Na_2S_2O_3}}{m} \quad (1)$$

Oxirane oxygen content was determined by direct method using hydrobromic acid solution in glacial acetic acid [21]. The following expression was used to calculate the percentage oxirane oxygen of the oil samples.

$$\text{OO (weight \%)} = \frac{1.6 \times V_{HBr} \times N_{HBr}}{m} \quad (2)$$

The relative percentage yield of epoxide was calculated using the following expression:

$$\text{Relative percentage yield of epoxide} = (\text{OO}_{exp}/\text{OO}_{the}) \times 100 \quad (3)$$

$$\text{where } \text{OO}_{the} = \left[\frac{(IV_0/2A_i)}{100 + (IV_0/2A_i)A_0} \right] A_0 \times 100 \quad (4)$$

α -Glycol content was determined by oxidation of glycol compound with benzyltrimethylammonium periodate in presence of a non-aqueous medium [22].

$$\text{Relative percentage yield of } \alpha\text{-glycol} = (G_{exp}/G_{the}) \times 100 \quad (5)$$

$$\text{where } G_{the} = \left[\frac{(IV_0/2A_i)}{100 + (IV_0/2A_i)2A_{OH}} \right] \times 100 \quad (6)$$

4. Instrumental Analysis

Fourier transform infrared (FTIR) spectroscopy analysis of nahor oil and ENO was performed using PerkinElmer Spectrum GX (model 4200) instrument to determine the presence of functional groups qualitatively. 1H -NMR spectra were recorded using Bruker AMX-500 FT NMR spectrometer to predict the presence of oxirane oxygen and C=C bond quantitatively. Brookfield made R/S Rheometer was used to measure the rheological property of cured epoxy resins. Texture Analyzer (Stable Micro Systems, UK) was used for testing the adhesive strength of the cured products.

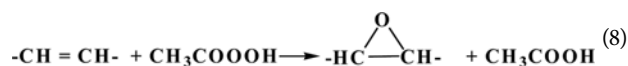
RESULTS AND DISCUSSION

To investigate the epoxide formation, epoxidation reactions were performed at a constant temperature of $50 \pm 1^\circ C$ in the presence of acid catalyst and oxygen carrier. The acid catalysts used for the reaction were H_2SO_4 , Amberlite IR 120H, and Dowex 50 WX8. The carboxylic acids, namely, acetic acid (AA), formic acid (FA), and propanoic acid (PA), were used as an oxygen carrier for the reaction. The reactions were carried out with an H_2O_2 -to-ethylenic unsaturation mole ratio of 2, and at a stirring speed of $1,600 \pm 25$ rev/min. Carboxylic acid-to-ethylenic unsaturation mole ratio of 0.4 was maintained for each run. Repeatability analysis shows that the deviation between two experimental results is less than 3%. The properties of oil, as experimentally determined are: specific gravity: 0.95 at $30^\circ C$; iodine value: 90 ± 1 (g I_2 /100 g oil); The fatty

acid composition of nahor oil as determined by gas chromatography mass spectrometry (model GCMS-QP2010, SHIMADZU) was: Palmitic acid ($C_{16:0}$): $7.5 \pm 1\%$; stearic acid ($C_{18:0}$): $11.3 \pm 1\%$; oleic acid ($C_{18:1}$): $54 \pm 1\%$; linoleic acid ($C_{18:2}$): $19 \pm 1\%$.

1. Epoxidation Reactions

A two-step process may be considered for the in-situ epoxidation reactions: (i) aqueous phase formation of peroxydicarboxylic acid by reacting between H_2O_2 and organic carboxylic acid in presence of acid catalyst, ii) reaction of peroxydicarboxylic acid with the unsaturated double bond to form epoxide in organic phase. Eqs. (7)-(8) show the two-step epoxidation reaction in the presence of acetic acid.



2. Comparison of Different Acid Catalysts on Epoxide Yield

To investigate the effect of acid catalysts on epoxide yield, epoxidation reactions were carried out with acetic acid in presence of three different acid catalysts, namely, H_2SO_4 , Amberlite IR 120H, and Dowex 50 WX8 under identical conditions. In each case, 48.7 g H_2O_2 , and 8.77 g CH_3COOH were treated with 100 g nahor oil at $50^\circ C$, at a stirring speed of 1,600 rev/min. Around 15 wt% (w.r.t. oil mass) catalyst loading was used for each acidic ion exchange resin catalyst. In case of H_2SO_4 catalyst, 2 wt% concentration (expressed as percentage of 'total weight of H_2O_2 and CH_3COOH added') was used for the reaction. The above-mentioned compositions were considered based on our previous experience about epoxidation reaction with different oil system.

Fig. 1 shows that the yield of epoxide increased with the increase of reaction time (within the experimental time limit) in the presence of both the acidic ion exchange resin catalysts. However, in the case of H_2SO_4 , epoxide yield initially increased with reaction time, attained a maximum value ($\approx 65\%$), and then started to decrease with time. Among the catalysts studied, Amberlite IR 120H showed the highest yield of epoxide as compared to Dowex 50 WX8 and H_2SO_4 . A maximum of 70% epoxide yield was obtained with Amberlite IR 120H at $50^\circ C$ after a reaction time of around 8 hrs.

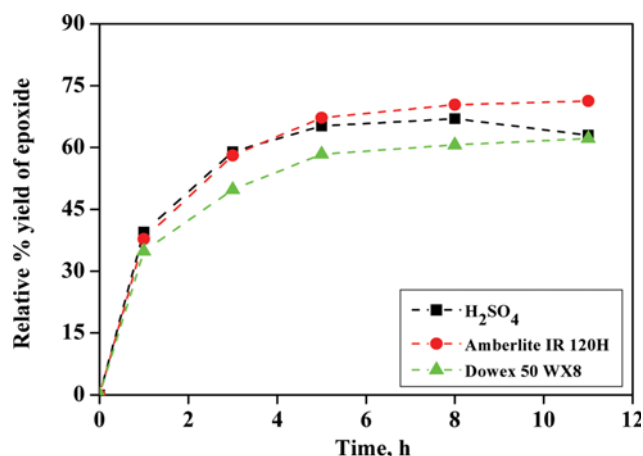


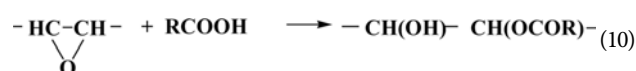
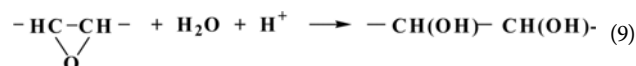
Fig. 1. Effect of catalyst on epoxide yield.

Table 1. Iodine value conversion and α -G yield with different catalysts

Catalyst	Properties	Time, h			
		3	5	8	11
H_2SO_4	% Conv. of IV	66.9	75.1	81.7	85.1
	% Epoxide yield	59.1	65.2	66.9	63.2
	% Yield of α -G	2.9	4.8	9.5	16.1
	% Yield of other by-product	4.9	5.1	5.3	5.8
Amberlite IR 120H	% Conv. of IV	64.1	73.5	79.2	83.2
	% Epoxide yield	58.1	67.2	70.4	71.3
	% Yield of α -G	1.7	1.8	3.9	6.9
	% Yield of other by-product	4.3	4.5	4.9	5
Dowex 50 WX8	% Conv. of IV	56.4	65.1	68.6	72.1
	% Epoxide yield	49.8	58.3	60.4	62.1
	% Yield of α -G	1.6	1.7	3.2	5.4
	% Yield of other by-product	5	5.1	5	4.6

Conditions: temp. = $50^\circ C$; H_2O_2 -to-EU mole ratio = 2; AA-to-EU mole ratio = 0.4

For H_2SO_4 , the decrease of epoxide yield with time is mainly due to the hydrolysis and other consecutive reactions of epoxide to glycol products. The yield of α -glycol (α -G) and iodine value conversion corresponding to epoxide yield with three different catalysts is tabulated in Table 1. The most probable ring cleavage reactions are shown by Eqs. (9)-(10).



Generally, for a homogeneous catalytic reaction, the rate of reaction always depends on the initial catalyst concentration. Hence, one may expect that the epoxide formation would increase with the increase of H_2SO_4 concentration. However, in the present study, H_2SO_4 not only catalyzed the formation of peroxydicarboxylic acid, but also it catalyzed the consecutive ring opening (e.g. hydrolysis) reactions of epoxide to glycol derivatives.

To investigate the reason for lower epoxide yield with Dowex 50 WX8 compared to Amberlite IR 120H, the ion (H^+) exchange capacity of both the catalysts was determined experimentally by chemical analysis. The experimentally determined H^+ ion exchange capacity of Dowex 50 WX8 is about 1.6 milliequivalent per gram of catalyst and the corresponding value for Amberlite IR 120H is about 2.1 milliequivalent per gram of catalyst. Therefore, the lower yield of epoxide with Dowex 50 WX8 may be due to its poor ion exchange capacity compared to Amberlite IR 120H catalyst.

3. Comparison of Different Carboxylic Acids on Epoxide Yield

To compare the effect of carboxylic acids on epoxide yield, epoxidation reactions were carried out with three different carboxylic acids: formic acid (FA), acetic acid (AA), and propanoic acid (PA) under identical conditions. In each case, 48.7 g H_2O_2 , and 15 g Amberlite IR 120H were treated with 100 g nahor oil at $50^\circ C$ tem-

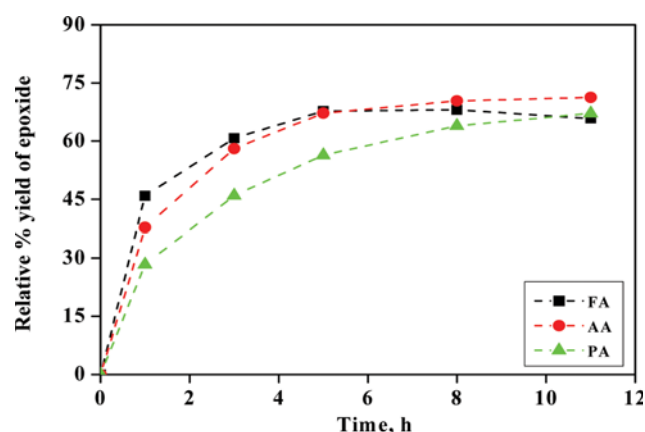


Fig. 2. Effect of carboxylic acid on epoxide yield.

perature under a stirring speed of 1,600 rev/min. Carboxylic acid-to-EU mole ratio of 0.4 was maintained for all three experiments, and the relevant results are shown in Fig. 2.

The figure shows that initially the epoxide conversion was relatively higher with FA as compared to AA or PA. The epoxide yields with FA, AA, and PA after 3 hrs of reaction were 61%, 57% & 46% respectively. However, as time progressed, epoxide yield started to decrease after reaching a maximum value of around 68%, whereas the iodine value conversion increased gradually with time in presence of FA. Conversely, in the case of AA and PA, both iodine value conversion and epoxide yield increased gradually within the experimental time limit. The result shows that, after 11 hrs of reaction, the epoxide yields were 71% and 67% with AA and PA, respectively. However, in the case of AA, no significant ($\approx 1\%$) change in epoxide yield was observed between 8 hrs and 11 hrs. The iodine value conversion and α -glycol yield correspond to the epoxide yield, given in Table 2.

The analysis also shows that the difference between iodine value

conversion and epoxide yield (at maximum epoxide yield) was higher (16.5%) in the case of FA than that of AA (11.9%) or PA (8.5%). This indicates that greater amounts of undesired products were formed in the presence of FA compared to the other two acids, and that was confirmed from the analysis of α -G values shown in Table 2. The order of effectiveness of carboxylic acids was found to be FA>AA>PA. The decreasing order of reactivity from FA to PA may be due to the gradual increase of positive inductive effect (+I) of $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ group attached to the carboxylic group in AA and PA, respectively. Eqs. (11)-(12) show the formation of percarboxylic acid from carboxylic acid and H_2O_2 in presence of H^+ ion.



The stability of R-COOOH_2^+ intermediate depends upon the 'R'-group attached to the $-\text{COOOH}_2^+$ group. For formic acid $\text{R} = \text{H}$, for acetic acid $\text{R} = \text{CH}_3$, and for propanoic acid $\text{R} = \text{C}_2\text{H}_5$. As +I effect of $-\text{C}_2\text{H}_5 > -\text{CH}_3 > -\text{H}$, hence, the stability order of $\text{C}_2\text{H}_5\text{-COOOH}_2^+ > \text{CH}_3\text{-COOOH}_2^+ > \text{H-COOH}_2^+$. The higher the stability of R-COOOH_2^+ intermediate, the lower is the rate of formation of percarboxylic acid (R-COOOH). Therefore, the rate of formation of $\text{C}_2\text{H}_5\text{-COOOH} < \text{CH}_3\text{-COOOH} < \text{H-COOOH}$ and consequently the rate of epoxidation with $\text{FA} > \text{AA} > \text{PA}$.

4. FTIR and NMR Analysis of Nahor Oil and Products

To identify the functional groups present in the nahor oil and epoxidized nahor oil (ENO), FTIR analysis was performed for both the oil and ENO samples. A typical FTIR spectrum of nahor oil and ENO sample is shown in Fig. 3. The iodine value conversion and epoxide yield of the ENO sample used for FTIR analysis were 83.2% and 71.3% respectively.

A characteristic band at about 1583 cm^{-1} (Fig. 3(a)) indicates the presence of $\text{C}=\text{C}$ bond in the nahor oil. There is no characteristic peak that corresponds to O-H group, and C-O (epoxide C-O) group at around 3400 cm^{-1} and 830 cm^{-1} , respectively, was found in Fig. 3(a). Conversely, a broad band at around 3429 cm^{-1} and a sharp band at around 830 cm^{-1} in Fig. 3(b) indicate the presence of O-H group and C-O group, respectively, in the ENO product. The characteristic band at 1740 cm^{-1} corresponds to C=O stretching. The presence of O-H group in the ENO sample (Fig. 3(b)) supports the

Table 2. Values of iodine value conversion and α -G yield with various carboxylic acids

Catalyst	Properties	Time, h			
		3	5	8	11
Formic acid (FA)	% Conv. of IV	68.9	78.3	84.7	86.9
	% Epoxide yield	60.7	67.8	68.1	65.8
	% Yield of α -G	4.2	6.8	11.8	16.2
	% Yield of other by-product	4.0	4.0	4.8	4.9
Acetic acid (AA)	% Conv. of IV	64.1	73.5	79.2	83.2
	% Epoxide yield	58.1	67.2	70.4	71.3
	% Yield of α -G	1.7	1.8	3.9	6.9
	% Yield of other by-product	4.3	4.5	4.9	5.0
Propanoic acid (PA)	% Conv. of IV	49.6	61.2	71.2	75.7
	% Epoxide yield	46.0	56.4	64.0	67.2
	% Yield of α -G	1.1	1.5	2.8	4.4
	% Yield of other by-product	2.5	3.3	4.4	4.1

Conditions: temp.=50 °C; Amberlite IR 120H loading=15 wt%; H_2O_2 -to-EU mole ratio=2; carboxylic acid-to-EU mole ratio=0.4

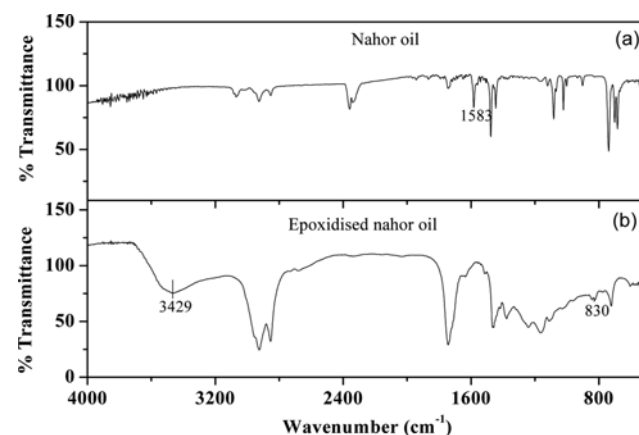


Fig. 3. FTIR spectra of (a) nahor oil; (b) epoxidised nahor oil (ENO).

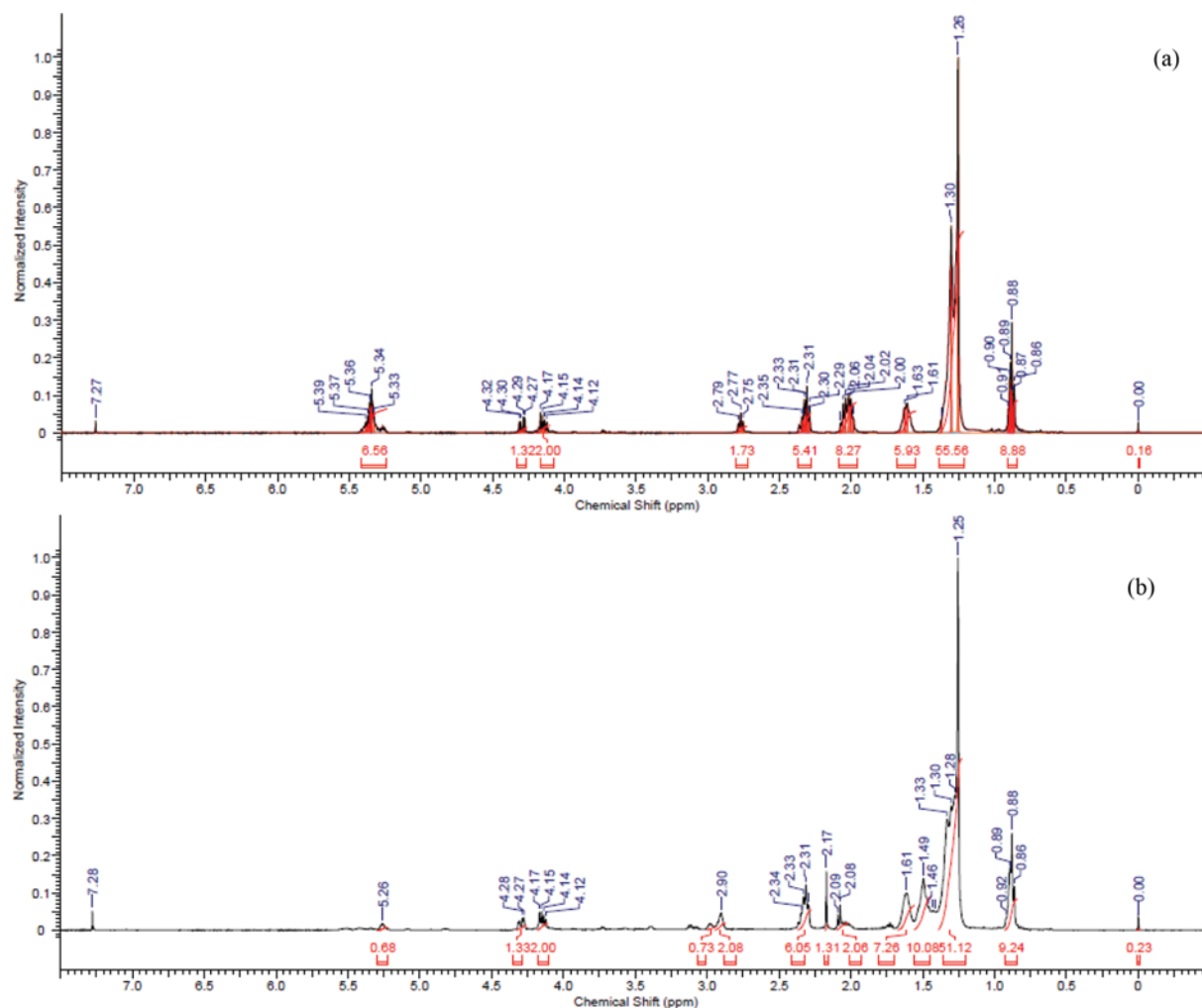


Fig. 4. ^1H NMR spectra of (a) nahor oil; (b) epoxidized nahor oil (ENO).

cleavage of epoxide ring during the course of reaction.

Fig. 4 shows the ^1H NMR spectrum of the nahor oil and ENO (same sample used for FTIR analysis). For the ^1H NMR analysis, both the samples were dissolved in CDCl_3 solvent. The peak at 7.27 ppm corresponds to the CDCl_3 solvent. The peaks between 5.25 and 5.45 ppm (Fig. 4(a)) indicate the presence of olefinic hydrogens ($\text{CH}=\text{CH}$) in nahor oil sample. The peaks mostly disappeared in the epoxidized nahor oil sample (Fig. 4(b)) and some new peak appeared at 2.9 ppm. The peaks between 2.85 and 2.95 ppm represent the C-H proton attached to the oxygen atom of epoxide group. Based on the peak area calculation, it has been found that the C=C double bond conversion was around 82% and it matched very well with the experimentally measured conversion (around 83%) based on the iodine value analysis. Therefore, ^1H NMR analysis confirmed two things for the present study: i) formation of epoxide bond from C=C double bond, and ii) percentage conversion of C=C double bond.

5. Curing of Epoxidized Nahor Oil (ENO)

To develop an epoxy resin from epoxidized nahor oil (ENO), a curing reaction was carried out with ENO and curing agent. Two curing agents, ethylenediamine (EDA) and diethylenetriamine (DETA),

were tested. To do the curing reaction, a measured amount (25 g) of purified ENO sample was taken into a glass reactor. Calculated amount (molar equivalent) of hardener (~ 0.9 g EDA or ~ 1.21 g DETA) was added into the reactor and the mixture was stirred at 500 rev/min for 30 min at around 70°C . Then the reacting mass was allowed to cool to room temperature ($\approx 30^\circ\text{C}$). After 12 hrs, the solidified mass was removed from the reactor, and then its various physico-chemical properties were analyzed.

6. Rheological Behavior of Cured Epoxy Resin

To study the rheological behavior of the cured epoxy resins, rheology tests were performed using the Brookfield R/S+ Rheometer. About 4 mL sample was loaded in the viscometer cup, and the shear rate was varied from 1 to 900 s^{-1} over a span of 60 sec at 30°C . Typical rheograms of cured epoxy resins and ENO sample are shown in Fig. 5. Fig. 5(a) shows the variation of viscosity, and share stress with share rate for ENO sample. To measure the viscosity of the solidified or highly viscous cured resins, samples were diluted with a fixed quantity (1 : 1 wt. ratio) of diluent. Chlorobenzene was used as a diluent for the present study. Fig. 5(b) and Fig. 5(c) show the variation of viscosity with share rate for EDA cured epoxy resin without, and with, dilution respectively. Fig. 5(d) represents a simi-

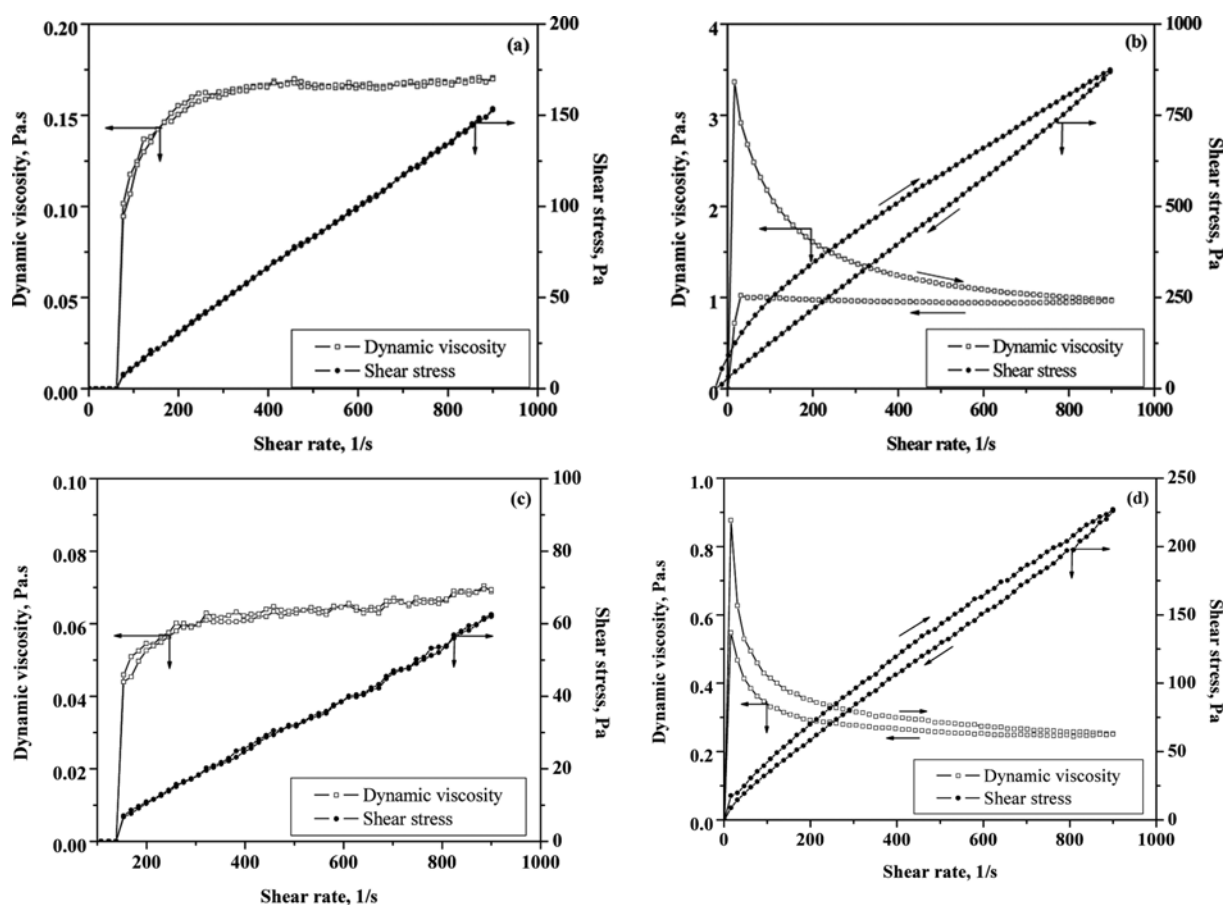


Fig. 5. Rheogram of ENO and amine cured epoxy resins: (a) ENO without dilution; (b) EDA-cured epoxy resin without dilution; (c) EDA-cured epoxy resin with dilution; (d) DETA-cured epoxy resin with dilution.

lar study for DETA cured epoxy resin with solvent dilution.

Fig. 5(a) shows that shear stress increases linearly with shear rate for ENO sample, whereas for the amine-cured resins, a non-linear behavior is observed with shear rate. The viscosity of the cured products (Fig. 5(b) and Fig. 5(d)) continuously decreases with the increase of shear rate and shows a shear thinning behavior. With the increase of shear rate, the cross-linked bonds opened and the material began to flow, showing a considerable decrease in viscosity. Therefore, based on the analysis, it can be said that the ENO sample behaves like a near Newtonian fluid. Whereas, both the amine-cured resins behave like a non-Newtonian thixotropic fluid under the present experimental condition. The area between the forward and backward direction represents the degree of thixotropic behavior. The estimated thixotropic value for EDA-cured resin (without diluent) was around $80,800 \text{ Pa s}^{-1}$. The average viscosity and thixotropic values of ENO, and cured resin samples are in Table 3.

The data shows that the average viscosity of EDA-cured resin

increased by around 9.2-fold compared to ENO sample, and the corresponding increment for DETA-cured resin is around 56.6 fold. DETA contains both primary and secondary amine groups and can act as tridentate chelating agent, whereas DEA acts as a bidentate ligand and contains only primary amine groups. Therefore, based on the above analysis, DETA acts as a more effective curing agent compared to EDA for the present study.

7. Adhesive Property of Cured Epoxy Resin (Tensile Test)

To study the adhesive behavior of the in-house developed cured epoxy resins, an adhesive strength test was performed using the Texture Analyzer. Cardboard surface was used to test the applicability of the cured resin as an adhesive. To prepare sample for adhesive strength test, cardboard material was cut into a dog bone shaped structure and joined in a lap shear mode with the middle portion of one substrate stuck to one-half of the other substrate using cured epoxy resins. The glued samples were kept aside for 24 hrs with 5 kg load on them to enhance the physico-chemical interaction

Table 3. Average viscosity value of ENO and amine cured resins at 30°C

	ENO without diluent	EDA-cured resin without diluent	EDA-cured resin with diluent	DETA-cured resin with diluent
Average viscosity, cP	148	1367	52	319
Thixotropic value, Pa s^{-1}	70	150	80800	9900

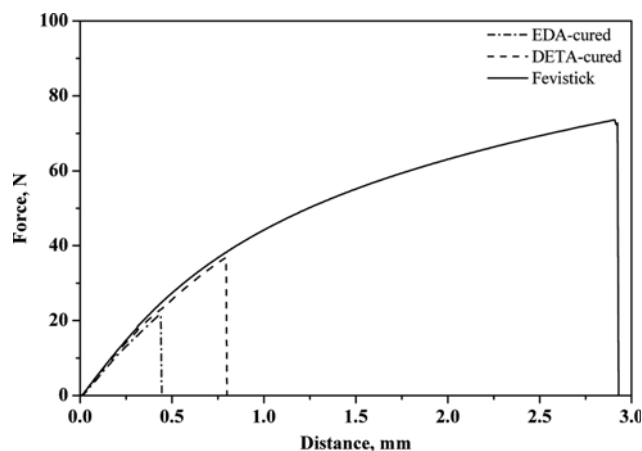


Fig. 6. Tensile strength of cardboard samples glued with amine-cured epoxy resins and fevistik.

between the resin and the cardboard surface before performing the tensile test. The cardboard sample was fixed between the tensile grips (coated with rubber to avoid the slippage). The test was performed with 2 mm/sec speed with a pre-test speed of 1 mm/sec under auto trigger mode. The results are shown in Fig. 6 along with the reference sample of commercially available fevistik glue.

The figure shows that the tensile force of DETA-cured resin is around 1.7-fold greater than that of EDA-cured resin, and the tensile force of the fevistik is around two-fold higher compared to DETA-cured resin. The force required to detach the cardboard sheet is directly proportional to the adhesiveness/stickiness behavior of the sticking material. In the present study, the force applied to break the cardboard joint was around 21.4 N and 36.3 N for EDA-cured and DETA-cured resin, respectively. The present work confirms that the bio-based cured epoxy resin could be used as an adhesive or glue for various applications.

CONCLUSIONS

The present study reveals that nahor oil could be epoxidized effectively by in-situ generated peroxyacid at a moderate temperature of 50 °C, and epoxidized oil could be further converted to an amine-cured epoxy resin. The suitability of different carboxylic acids--formic acid, acetic acid, and propanoic acid on epoxidation reaction--was examined in the present study. The effectiveness of carboxylic acids was found to be in the order of formic acid>acetic acid>propanoic acid. The effect of different acid catalysts--H₂SO₄, Amberlite IR 120H, and Dowex 50 WX8 on epoxide yield--was examined. Amberlite IR 120H shows better epoxide yield compared to H₂SO₄ and Dowex 50 WX8. It was possible to obtain around 70% epoxide yield within 8 hrs of reaction at 50 °C. The FTIR and NMR analysis confirmed the formation of glycol product during the course of reaction. An attempt was made to prepare a cured epoxy resin from epoxidized nahor oil (ENO). Curing reactions were performed with ENO and ethylenediamine (EDA) or diethylenetriamine (DETA) as a curing agent at 80 °C. The adhesive property of the cured resins was tested on cardboard material. The test shows that the bio-based cured epoxy resin could be used as

an adhesive for sticking cardboard materials. The force required to break the cardboard joint was around 36.3 N for DETA-cured epoxy resin vis-à-vis the corresponding value was 73.6 N for the fevistik material (commercial glue). The findings of the present study provide useful information for developing a bio-based lubricant (epoxidized oil) and adhesive (cured epoxy resin).

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NOMENCLATURE

- A_0 : atomic weight of oxygen [g mol^{-1}]
- A_{OH} : atomic weight of hydroxyl group [g mol^{-1}]
- A_i : atomic weight of iodine [g mol^{-1}]
- EU : ethylenic unsaturation
- G_{exp} : experimentally obtained α -glycol [mole/100 g sample]
- G_{the} : theoretically obtainable maximum α -glycol [mole/100 g sample]
- IV_0 : initial iodine value [$\text{g of I}_2/100 \text{ g sample}$]
- N : normality
- OO_{exp} : experimentally obtained epoxide oxygen [$\text{g}/100 \text{ g oil sample}$]
- OO_{the} : theoretically obtainable maximum epoxide oxygen [$\text{g}/100 \text{ g oil sample}$]
- V_B : volume of sodium thisulphate solution consumed by blank titration [mL]
- V_S : volume of sodium thisulphate solution consumed by the oil sample [mL]
- V_{HBr} : volume of HBr [mL]
- m : mass of sample [g]

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