



Producing Phosphate-Polyols by Ring-Opening Hydrolysis of Wild Safflower Oil Epoxides

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Abstract : This work present the methodology for preparing epoxidized wild safflower oil (EWSO) using cation exchange resin as heterogeneous catalyst and its subsequent ring-opening hydrolysis in presence of phosphoric acid under varying experimental parameters. The influence of various reaction conditions such as type and relative ratio of solvent, phosphoric acid dosing and water content on the ring-opening response was investigated. The hydrolyzed products, WSO-phosphate polyols were analytically characterized for hydroxyl content, oxirane content, acid value and viscosity. The chemical confirmation of the synthesized polyols was done using FTIR spectral analysis. The rate of degradation of oxirane rings in acid hydrolysis of EWSO was moderately rapid in aqueous acid media, when *t*-butyl acetate used as solvent, with higher hydroxyl value of the derived polyols.

Keywords : Wild safflower oil, epoxidation, oxirane content, ring-opening, polyols.

Introduction

Vegetable oils and fats are the important renewable resources and are nowadays increasingly replacing petroleum derived materials in various fields as they are biodegradable, low in cost and readily available. Vegetable oils and their derivatives can serve as a feedstock for many applications such as fuels (bio-diesel)¹, polymers²⁻³, lubricants⁴⁻⁵, surfactants⁶⁻⁷, plasticizers⁸ and specialty chemicals⁹. Thus, there is an immediate need of attention towards effective utilization of these bio-based products taking into the consideration of current environmental harm and steadily rising petroleum prices. Moreover, this trend will promote the sustainable agricultural initiative.

Epoxidation is one of the most important reactions that introduce the high strain energy three-membered oxirane ring into the unsaturated part of the natural oil. The newly attached epoxide groups in triglyceride structure being highly reactive make them to be readily transformed into desired functionality. The chemistry of epoxidation of unsaturated fatty compounds is well known and usually involves peracid formation by reaction with molecular oxygen or hydrogen peroxide either in a separate step or *in situ*¹⁰. Industrially epoxides have been prepared from castor, linseed, rapeseed, soybean and sunflower oils containing high to moderate unsaturation. The utilization of other seed oils of semidrying nature like canola¹¹, karanja¹², jatropha¹³, rubber seed¹⁴, cottonseed¹⁵, mahua¹⁶ etc for epoxide synthesis have also been reported. Safflower is an important oilseed crop of the tropical countries, of which most species are wild and weed. Wild safflower oil (WSO) consists of a mixture of triglycerides derived mostly from C₁₆ to C₁₈ saturated and unsaturated fatty acids¹⁷. However, taking into account of higher proportion of unsaturation in fatty acid composition of the WSO, it is characterized as semidrying¹⁸ and therefore, can be used as renewable relatively inexpensive resource in preparation of epoxides.

Epoxidized vegetable oils are currently used on industrial scale as plasticizers for polyvinyl chloride, reactivdiluent and toughening materials for epoxy resins. Besides, epoxidized oils can be modified through the ring-opening of oxirane groups using nucleophilic reactions with alcohols¹⁹⁻²¹, acids²²⁻²³, water²⁴ or via hydrogenation²⁵ to obtain polyols having multiple hydroxyl functional groups. These biobased polyols are reported to have application in electroinsulating casting compounds²⁶ and, serve as the most predominant reactant replacing the conventional petrochemical-based polyol, reacting with isocyanates to produce polyurethane foams, elastomers, and coatings²⁰. The other possible synthesis routes to obtain polyols from vegetable oils are hydroformylation, ozonolysis, transesterification, metathesis and alkoxy-carbonylation, and thiol-ene coupling²⁷. However, some deliberate attempts have been made to study the ring-opening hydrolysis of epoxides with polar solvent in presence of phosphoric acid to prepare soy-based phosphate polyols^{23,28} and reported to improve the corrosion resistance property in coating applications.

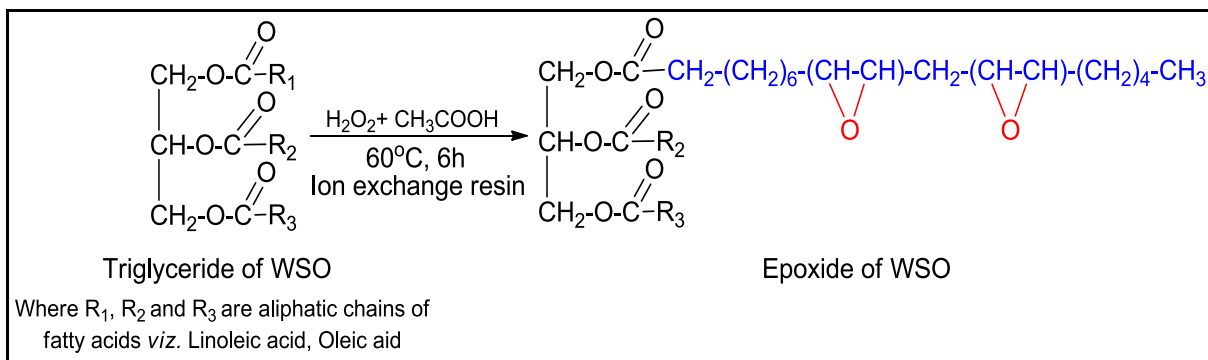
In present work, we report epoxidation of wild safflower oil (EWSO) using cation exchange resin as a catalyst and investigate the effects of catalyst, solvent and the amount of water on the ring-opening hydrolysis of synthesized EWSO. The hydrolyzed products, WSO-phosphate polyols were analytically tested for different properties by standard laboratory methods and analyzed using FTIR spectroscopy.

Materials and Methods

About 10 Kg seeds of wild safflower (*Carthamus oxyacantha*) were collected from the adjoining regions of Punjab district and extracted according to AOCS Official Method Ba 3-38 with Rankosolv SG solvent (distillation range 63.0-70.0°C; water content, as determined by KF method, 0.1%) obtained from Rankem RFCL, New Delhi, India. The seed yielded 28.6% (wt basis) of crude yellow oil, which was purified, refined and bleached by usual methods. Refined WSO, after due analytical study, was used for further experimentation. The laboratory grade chemicals glacial acetic acid (98%) and *o*-phosphoric acid (PA, 85%) were obtained from Qualigens India Ltd., Mumbai, India. AR grade hydrogen peroxide (30 wt%), Iodine monochloride and Wj's solution were procured from S.D. Fine Chemicals Ltd., Mumbai, India. HBr in acetic acid (33 wt%) was obtained from Fischer Scientific, Mumbai, India and then diluted with glacial acetic acid to make 0.1N HBr. The other chemicals, solvents and reagents used in the study were of LR grade and procured from CDH Ltd., Mumbai, India. Strongly acidic cation exchange resin, Amberlite® IR-122 (sulfonic acid functionality, 16-50 wet mesh size, macroreticular form) with a total cation exchange capacity 2.1 meq/mL was procured from Sigma-Aldrich (USA).

Preparation of WSO epoxide

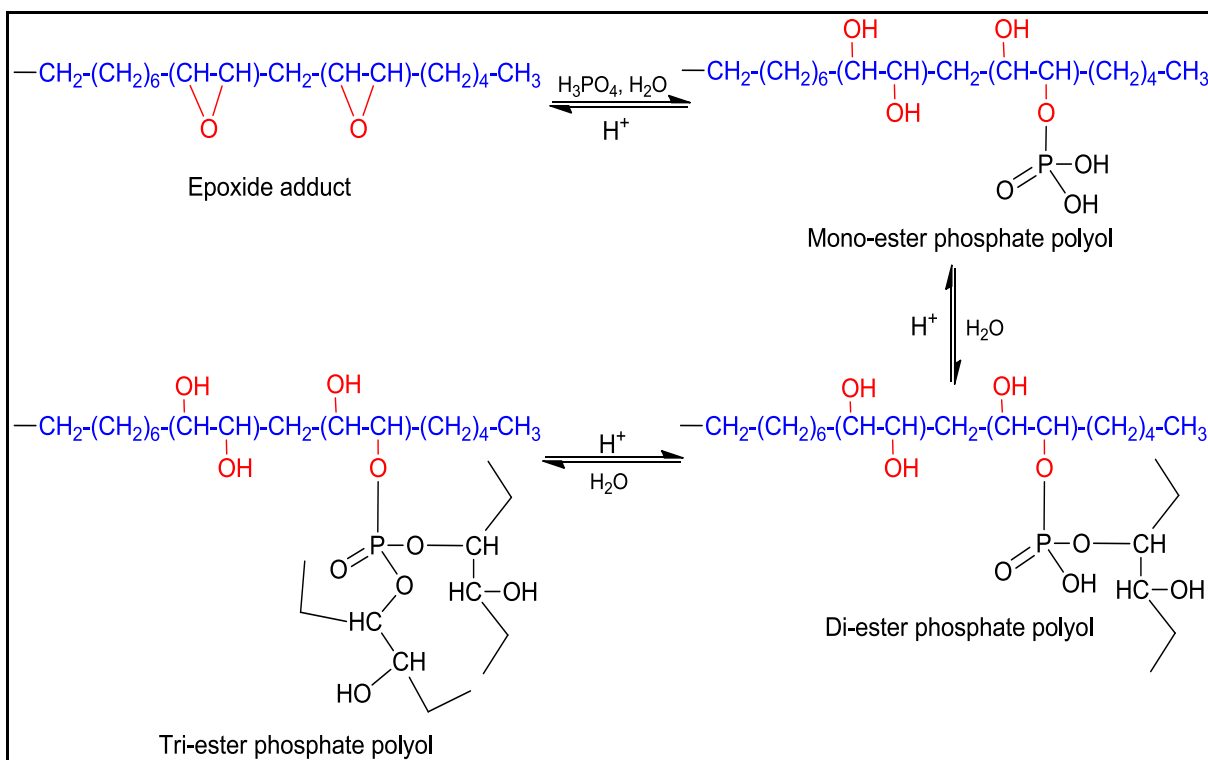
The batch mode epoxidation of WSO was carried out in a glass reactor consisting of a four-neck round bottom flask of 2 L capacity fitted with mechanical stirrer, temperature measuring device, dropping funnel and condenser. The reactor assembly was placed in a thermostatic oil bath equipped with controller to maintain the system temperature within ± 2 °C. A calculated amount of WSO was introduced in the reactor and heated at constant stirring (800 rpm) upto 40°C for 15 min. The requisite amount of acetic acid and catalyst (20 wt %) was added and the mixture was continuously stirred for next 30 min. This was followed by dropwise addition of hydrogen peroxide (1.5 mole per mole of ethylenic unsaturation) over a period of 30 min under continuous stirring with gradual increase in temperature upto 60°C and the reaction was continued for next six hours (Scheme 1). At the end of reaction, heating was stopped and stirring was continued till temperature of the product cool down to room temperature. The derived epoxide product was extracted with diethyl ether followed by successive washing with warm water to make it acid free. The upper ethereal layer was separated and the solvent was evaporated in rotary vacuum evaporator to obtain pure EWSO. The dried epoxide sample was analyzed for oxirane content and iodine value.



Scheme 1: Epoxide synthesis reaction from wild safflower oil (WSO)

Ring-opening hydrolysis of EWSO

The above prepared EWSO was used to study the oxirane ring-opening using acid hydrolysis route. The hydrolysis experiments were performed as per the procedure reported in literature²³. Briefly, a requisite amount of EWSO was dissolved separately in a portion of reaction solvent and the remaining amount of solvent along with PA and water, in a specified proportion, was charged into the fully baffled glass reactor. The reaction mixture was brought to the reflux condition by heating at the slow rate under constant stirring. The temperature of the reaction mixture was in the range of 60-120 °C depending upon the choice of solvent. The prepared slurry of EWSO in solvent was then added dropwise into the reactor over a period of 30 min. After the complete addition of EWSO slurry, the reaction was continued for next five hours under continuous stirring, to ensure fine dispersion of the epoxide. The course of the hydrolysis reaction was followed by withdrawing samples at regular intervals. The collected samples were purified to make them acid free by washing its ethereal extract (1:1 v/v) with deionized water to enhance the separation of the oil product from water phase, and dried in a rotary vacuum evaporator. The extent of hydrolysis was monitored by determination of the oxirane content of the washed aliquots of the reaction mixture.



Scheme 2: Synthesis route for WSO-phosphate polyol by ring-opening hydrolysis

Analytical and instrumental methods

Acid value (A.V.), saponification value (S.V.), iodine value (I.V.) and specific gravity (Sp. Gr.) of the refined WSO were determined according to AOCS Method Cd 3d-63, AOCS Method Cd 3-25, AOCS Method Cd 1b-87 and MS 817:1989 respectively. The extracted WSO was subjected to gas chromatography to find out the fatty acid composition. WSO ester sample was analyzed with Shimadzu GC-14B gas chromatograph using Chromatopack Silar 10C column (12 m x 0.53 mm ID x 0.31 μm). The samples were injected at port temperature 230°C with N_2 carrier gas flow of 10 mL/min using FID detector maintained at 270°C. The oven was programmed from an initial temperature of 180°C to 200°C at heating ramp of 2°C/min with a 5 min hold, raised to 230°C at 7°C/min and kept for 5 min, then upgraded to 250°C at 7°C/min with a 2 min hold for a total run time of 20 min.

The percent oxirane oxygen content of the prepared WSO-phosphate polyols was determined using AOCS Official Method Cd 9-57 (1997) in which the oxygen was titrated directly with HBr solution in acetic acid. Hydroxyl value (H.V.) and acid value (A.V.) of the polyol samples were determined by standard methods of ASTM D-1639-90 (1996) and AOCS Tx 1a-66 (1997) respectively. The viscosity was measured using SV-10 sine wave vibroviscometer (A&D make, Tokyo, Japan) at 30°C. The vibrational changes in the structural functional groups of WSO-phosphate polyol samples were characterized with FTIR spectra, measured on Shimadzu FTIR-8400 spectrometer in the range of 4000 to 400 cm^{-1} .

Results and Discussion

The properties of WSO with fatty acid composition were obtained as follows: Sp. Gr. = 0.918 (at 25°C); A.V. (mg KOH/g) = 0.2; I.V. (g I_2 /100 g) = 146; S.V. (mg KOH/g) = 192; oleic acid, $\text{C}_{18:1}$ = 12.6%; linoleic acid, $\text{C}_{18:2}$ = 70.5%. *In situ* epoxidation reaction was carried out with 1:0.5:1.5 molar ratio of ethylenic unsaturation: acetic acid: hydrogen peroxide at 60°C. In epoxidation reaction, acetic acid was converted to peracetic acid and was constantly being regenerated, an excess of 0.5 mole relative to ethylenic unsaturation was considered reasonable. The theoretical maximum oxirane content in 100 g of oil was calculated to be 8.42%. Under the experimental epoxidation conditions, 7.87% oxirane content in prepared ESWO was obtained. The reduction in I.V. was achieved to 13.5 (g I_2 /100 g) with A.V. of 0.12 (mg KOH/g).

In present work, the phosphoric acid being a polybasic acid not only catalyze the ring-opening hydrolysis of EWSO with water but also expected that PA chemically bind with EWSO to produce mono-, di-, and tri-phosphate esters (Scheme 2). The presence of phosphate ester functionality in hydrolyzed product, WSO-polyol is desired to improve corrosion resistance and fire retardant properties, when used in coating applications. However, the extent of formation and hydrolysis of phosphate esters depends on several factors including relative nucleophilicity of reactants, stability of intermediates, solvent, temperature, and relative concentration of reactants²³. Therefore, we have investigated the effect of different solvents and varying the relative ratio of solvent, water and phosphoric acid on ring-opening reaction and studied the characteristics of the resultant WSO-phosphate polyols.

Effect of solvent :

The effect of solvents during hydrolysis reaction on the reduction of oxirane content was determined using five different solvents: acetone, tetrahydrofuran (THF), Isopropanol (IPA), ethyl acetate (EA) and *t*-butyl alcohol (TBA). In each case, EWSO was treated with PA-2%, solvent-50% and water-10% on weight basis. The characteristics of WSO-phosphate polyols obtained at the end of hydrolysis are presented in Table 1.

Table 1: Properties of WSO-phosphate polyols using different solvents

Parameter	Solvents				
	Acetone	THF	IPA	EA	TBA
EWSO/solvent (w/w)	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5
Phosphoric acid (%)	2	2	2	2	2
Water (%)	10	10	10	10	10
Oxirane content (%)	2.9	2.2	1.4	1.0	0.28
Acid value (mg KOH/g)	1.2	1.9	2.4	55	3.2
Hydroxyl value (mg KOH/g)	95	123	169	234	270
Viscosity (cPs, 30 °C)	3200	3540	4560	3890	3490

The extent of ring-opening during hydrolysis was monitored by determination of the percent oxirane content over the course of reaction time at regular time intervals. This variation of the percent oxirane content with reaction time for different solvents is depicted in Fig.1. The use of acetone and THF as solvent during hydrolysis showed depletion of oxirane content in the hydrolyzed products to 2.90 and 2.22 at the end of reaction, which corresponds to approximately 63.1% and 71.8% completion of the reaction, respectively. The higher rate of oxirane ring degradation (81.7 % conversion) was achieved in the polyol product based on IPA than that for acetone and THF, signified by the percent of residual epoxy groups in their products. EA as solvent resulted into 87.2% ring-opening, while for the product based on TBA a much faster rate of depletion of oxirane groups was observed, which indicated the higher rate of hydrolytic rupture. A very high A.V. (55 mg KOH/g) of the hydrolyzed product was found using EA as solvent. This can be attributed to the possible acid catalysis of this ester-type solvent in the presence of water, resulting in the formation of ethanol and acetic acid. From Table 1, it is evident that TBA was the best solvent for EWSO hydrolysis, since the degradation rate of oxirane ring was moderately swift in aqueous acid media (96.4 % conversion) along with a higher hydroxyl value (270 mg KOH/g) of the derived product. The relatively low nucleophilicity of TBA solvent system tends to rearrange its thermodynamically stable ion by multiple migrations and in turn responsible for a higher degree of hydrolysis. Therefore, further experiments were performed with TBA to study the effect of other parameters on oxirane ring-opening.

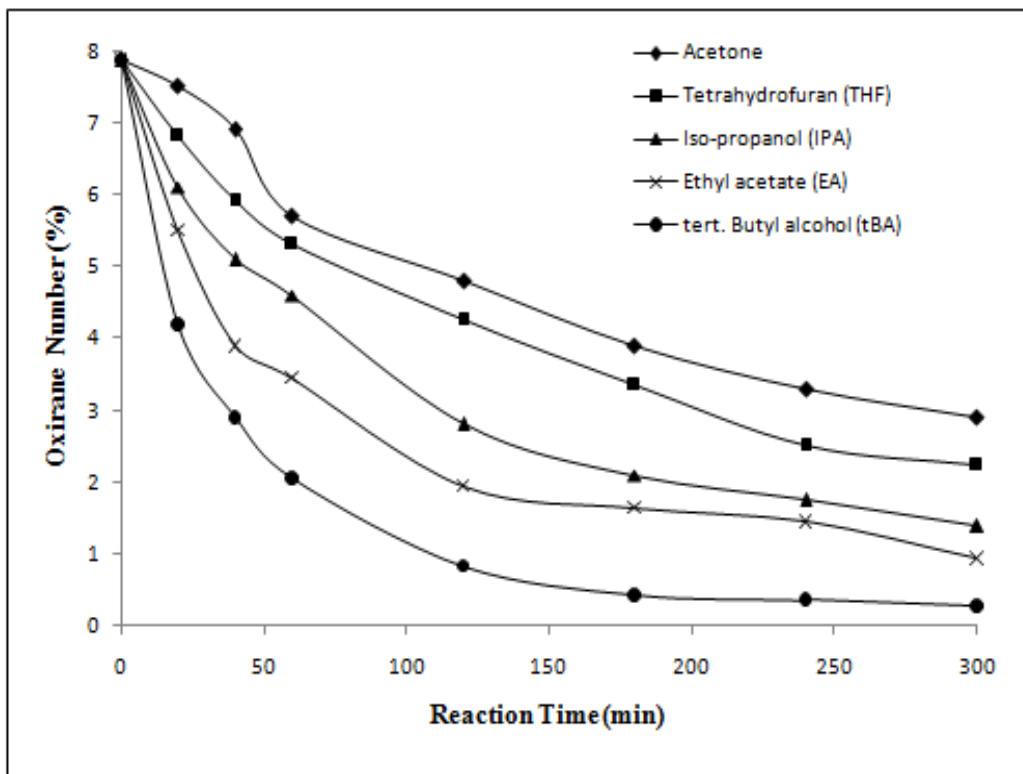


Fig. 1: Degree of hydrolysis of EWSO in different solvents a function of reaction time.

Effect of TBA dose :

The solvent dosing is an important parameter because this factor substantially affects the oxirane ring-opening. The influence of relative solvent ratio on the rate of reaction was investigated by performing hydrolysis at four different TBA concentrations of 0.2, 0.5, 1.0 and 1.5 wt% in the reaction mixture. The effect of varying TBA concentrations on the percent oxirane content is presented in Fig.2, which shows a gradual decline in oxirane content in the hydrolyzed product with increased EWSO dilution with TBA. An addition of 1.0% TBA in a reaction mixture enabled to reduce the oxirane content to 1.30%. However, there was no significant difference obtained for oxirane ring-opening capability beyond 0.5% TBA under the given conditions. Moreover, using 0.5 % TBA formed the product with substantial H.V. (270 mg KOH/g) at the end reaction. Therefore, 0.5% TBA concentration was considered to be optimum for subsequent hydrolysis experiments.

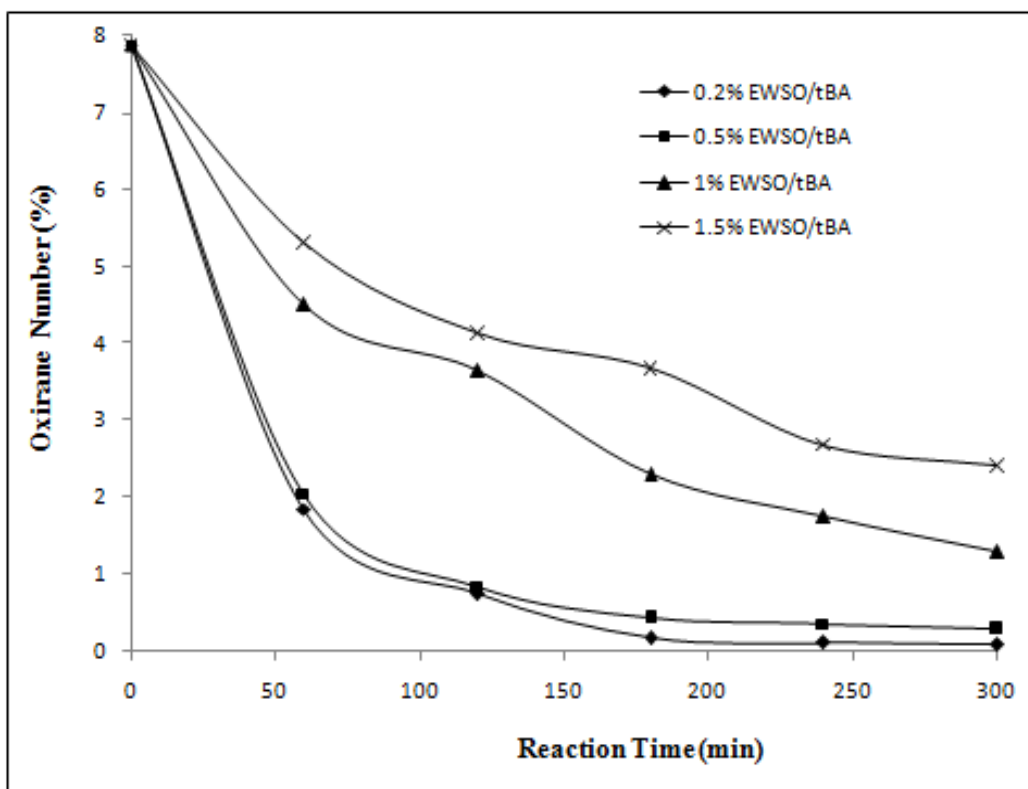


Fig. 2:Effect of relative solvent dosing on degree of hydrolysis of EWSO.

Table 2: Characteristics of WSO-phosphate polyols prepared using various reaction blends

Parameter	Solvent, <i>t</i> -butyl alcohol									
	1.0/0.2	1.0/0.5	1.0/1.0	1.0/1.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5
EWSO/solvent (w/w)	1.0/0.2	1.0/0.5	1.0/1.0	1.0/1.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5	1.0/0.5
Phosphoric acid (%)	2	2	2	2	3	4	5	10	2	2
Water (%)	10	10	10	10	10	10	10	10	20	30
Oxirane content (%)	0.08	0.28	1.3	2.4	0.18	0.11	0.06	0.02	0.08	0.05
Acid value (mg KOH/g)	9.2	3.2	2.85	2.15	10.8	31.2	68.8	118.2	2.95	2.6
Hydroxyl value (mg KOH/g)	256	270	245	218	241	248	259	275	275	279
Viscosity (cPs, 30 °C)	3650	3490	2460	1550	4160	4550	4780	3160	3360	3270

Concentration of phosphoric acid

PA plays a significant role in hydrolysis of the oxirane ring due to acidcatalyzed behavior of the reaction. The influence of PA concentration varied from 2 to 10% on the relative rate of ring-opening is shown in Table 2. The increase in PA content lead to absolute ring-opening indicated by the increasing trend in hydroxyl values of the product. At the same time, the products exhibited higher final acid values that can be attributed to the progressive hydrolysis of higher phosphate esters to lower esters²³. The viscosity of the hydrolyzed products

swiftly shoots as a function of PA content up to 5%. This might be due to presence of increasing amounts of higher phosphate esters. The product obtained with 10% PA dosing showed the higher hydroxyl value but comparatively reduced viscosity. This can be related to the availability of less higher phosphate esters resulted from the reduced rate of possible oligomerization during the course of reaction²³. At a higher acid concentration, there is the rapid utilization of oxirane groups in the formation of phosphate esters resulting in a significant drop in oligomerization.

Concentration of water

The influence of water content on the oxirane ring-opening *via* acid hydrolysis was investigated. From Table 2, it can be seen that increase in the concentration of water from 10% to 30% does not contribute any noteworthy effect besides a small increase in the rate of hydrolysis was evident.

Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectra of the WSO and epoxide adduct (EWSO) are shown in Fig. 3. For WSO the characteristic peaks at 3008 cm^{-1} , 1650 cm^{-1} and 721 cm^{-1} are attributed to the stretching vibration of the double bonds: =C-H, C=C, *cis*-CH=CH, respectively.

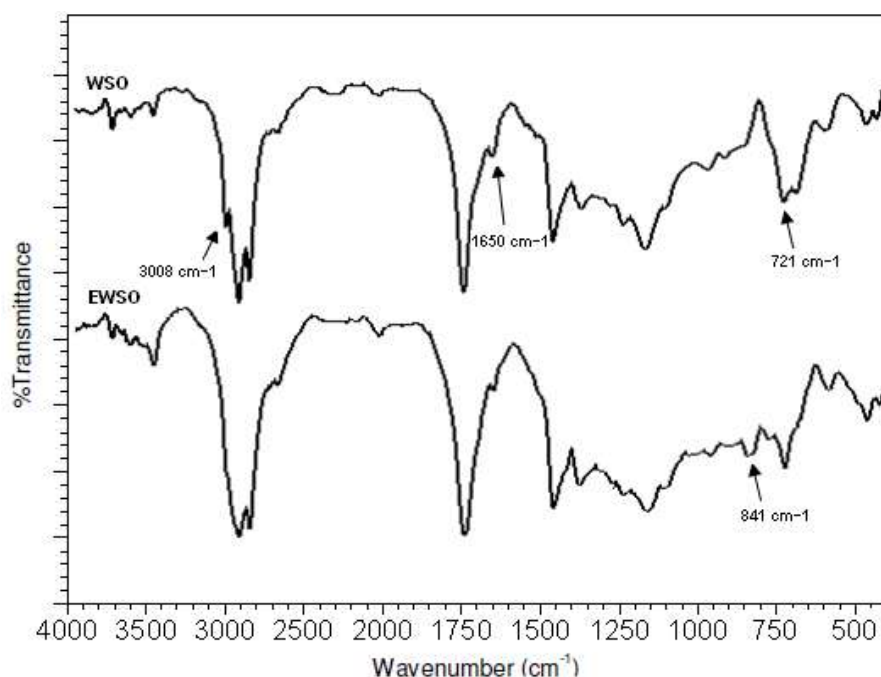


Fig. 3: FTIR spectra of WSO and EWSO.

Upon epoxidation the almost complete disappearance of double bonds band at 3008 cm^{-1} was observed and formation of new peaks at 841 cm^{-1} , ascribed to the epoxy groups, confirmed that almost all the C=C-H had taken part in the epoxidation reaction. The subsequent acid catalyzed epoxy ring-opening was monitored for the disappearance of characteristic peaks of EWSO and formation of other new peaks appearing at $3397\text{--}3410\text{ cm}^{-1}$, assigned to the hydroxyl functional groups and at $1075\text{--}1084\text{ cm}^{-1}$, phosphate ester groups (Fig.4).

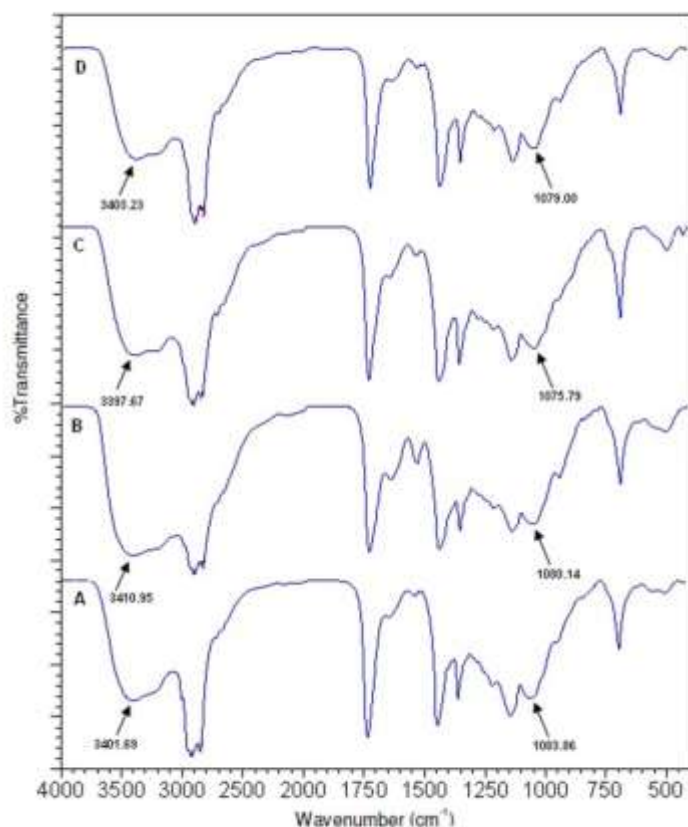


Fig. 4: FTIR spectrum of EWSO-PA2% polyol (A), EWSO-PA3% polyol (B), EWSO-PA5% polyol (C) and EWSO-PA10% polyol (D) (Conditions: Temperature, 60 °C; Reaction time, 5 hours; EWSO:TBA, 1:0.5; Water content, 10 %).

Conclusions

The epoxide adduct, EWSO was successfully synthesized by epoxidation using peroxy acid generated *in situ*. The acid catalyzed ring-opening hydrolysis of EWSO formed the WSO-phosphate polyols that showed variation in hydroxyl values. The completion of the reaction was judged and confirmed with the formation of single layer viscous product and FTIR analysis. The viscosity of the resultant product increased with the increase in PA concentration, suggesting the formation of phosphate esters from the appearance of IR absorption band at 1075-1084 cm^{-1} . The synthesized EWSO and WSO-phosphate polyols can serve as the potential intermediates for the producing various industrially important products.

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