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Polymer-grafted sulfonated carbon-catalyzed synthesis of α-hydroxy ethers as bio-lubricants from waste vegetable oil

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Abstract

The present paper describes the use of an easily accessible polymer-grafted sulfonated carbon composite catalyst for the synthesis of α-hydroxy ethers as bio-lubricants from waste vegetable oil via chemical modification involving esterification, epoxidation, and ring-opening reaction. A variety of α-hydroxy ethers were synthesized using different fatty alcohols for the evaluation of physicochemical properties. The bio-lubricants synthesized from 2-ethyl hexanol and dodecanol were found to be most promising as they exhibited lower pour point ($< -27\,°C$) and higher viscosity index (VI) 97 and 143, respectively. High VI and a lower pour point indicate ROP-3 and ROP-5 to be the most promising candidates as bio-lubricant for various applications.

Keywords Physicochemical property · Waste vegetable oil · Bio-lubricant · α-Hydroxy ethers · Pour point · Heterogeneous catalyst

1 Introduction

The growing concern for the environment leads to the use of renewable feedstocks such as vegetable oils and their derivatives for various applications including as fuels, lubricants, emulsifiers, plasticizers, surfactants, plastics, and solvents [1]. Owing to their easy availability, biodegradability, and environmentally friendly behavior, vegetable oils and derivatives have been considered as promising base stocks/formulation(s) for eco-friendly lubricants [2]. Their unique properties such as better lubricity, low volatility,

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high viscosity index, and high flash point make them as suitable solvents for fluid additives. However, the presence of unsaturation leads to poor oxidative and thermal stability [3]. Several attempts have been made to improve their oxidative stability [4–6] such as transesterification of rapeseed oil methyl ester with trimethylolpropane [7], selective hydrogenation [8, 9], and epoxidation [10–12]. In particular, epoxidation has found considerable interest owing to the higher reactivity of the oxirane ring for the further modification possibilities [13, 14]. Oxirane ring due to the ring strain can readily undergo to ring-opening reactions with nucleophiles to produce various valuable chemicals such as mono-alcohols, diols, alkoxy alcohols, hydroxy esters, N-hydroxyalkyl amides, mercapto alcohols, amino alcohols, and hydroxy nitrile [15, 16]. Ring-opening reactions are generally carried out in the presence of the acid catalyst, such as sulfuric acid, acetic acid, and p-toluene sulfonic acid [17]. However, corrosivity and tedious recovery of these homogeneous acidic catalysts make them unacceptable for practical applications. Subsequently, heterogeneous catalysts such as acidic ion exchange resins like Amberlyst 15 (dry) and Amberlite122R have been used, which offer several advantages such as low cost, easy availability, facile recovery, and recyclability. However, poor thermal stability and lower physical strength at higher temperature make their applicability limited.

In recent years, sulfonated carbon composites obtained from readily available bio-derived sources such as natural sugars have gained considerable interest as solid acid catalysts

for acid-catalyzed reactions [18–21]. These sulfonated carbon composites have hitherto been known for esterification [22, 23] and alkylation reactions [24]; however, no report is known for the oxirane ring opening of lubricant range esters.

We report herein an efficient ring opening of oxiranes by fatty alcohols for the synthesis of a series of α-hydroxy ethers to be used as bio-lubricants in the presence of polymer-grafted sulfonated carbon composite (P–C–SO₃H) as a heterogeneous acid catalyst. The reaction mainly consists of esterification, epoxidation, followed by oxirane ring opening (Scheme 1).

2 Experimental section

2.1 Materials and methods

All the substrates and reagents used were of analytical grade and used as received. Fatty alcohols (99%), oleic acid (~85%), formic acid (98–100%), and H_2O_2 (30 wt% in water) were procured from Merck, India. Acid oil was procured from a local vendor, Dehradun, India. The polymer-grafted sulfonated carbon composite (P–C–SO₃H) was synthesized by following the reported procedure [22, 23]. Sulfur content of polymer impregnated sulfonated carbon composite P–C–SO₃H was found to be 2.44 mmol H^+ per g as determined by elemental analysis assuming that all the sulfur atoms are presented in –SO₃H form. Further, acid site densities as calculated by using standard acid-base back titration method were found to be 2.54 mmol H^+ per g of catalyst. The slightly

higher value in comparison with the estimated values from elemental sulfur analysis might be due to the formation of phenolic-OH and –COOH groups resulting from the incomplete carbonization of glucose during the catalyst synthesis. The detailed synthetic methodology and characterization of the synthesized P–C–SO₃H catalyst are given in the supporting information (Figs. S1–S3).

2.2 Esterification of oleic acid and acid oil

The esterification was carried out by using oleic acid (20 mmol), 2-ethylhexanol (20 mmol), and tetramethylguanidine hydrogen sulfate (TMG.HSO₄) catalyst (5 wt% of total weight) [25] into a round-bottomed flask, and the resulting mixture were heated at 150 °C for 6 h under stirring. The reaction progress was monitored by thin-layer chromatography (TLC) using silica gel (SiO₂). After completion of the reaction, the organic layer was washed with petroleum ether, dried over anhydrous MgSO₄, and concentrated under reduced pressure to give the corresponding ester (2-ethylhexyl oleate). Conversion of acid to ester was calculated by employing the acid value (AV). The acid value of the sample was determined by the acid-base titration method. The FFA conversion (reduction in acid value) was calculated using the following equation:

$$X_{FFA} = a_i - a_t / a_i$$

where a_i is the initial acidity and a_t is the acidity at time t (6 h). Further, the crude product was purified by percolation through
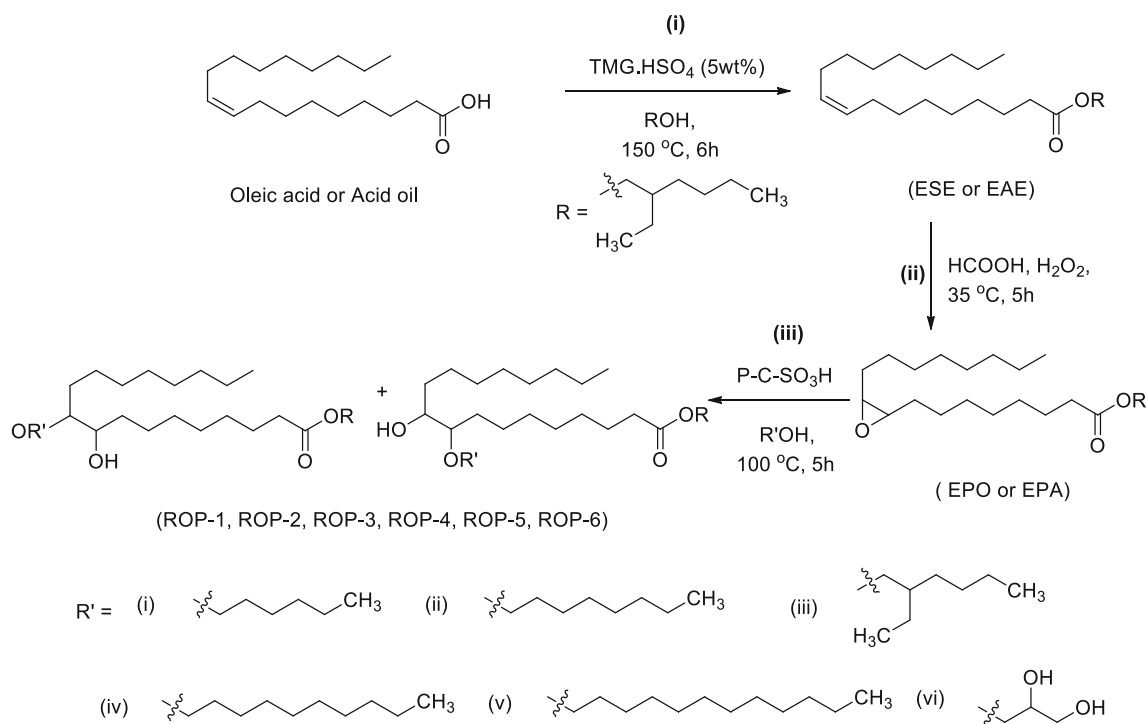
Scheme 1 Schematic representation for the synthesis of α-hydroxy ethers

basic alumina. After purification, the product was analyzed by ^{1}H and ^{13}C NMR.

Further, to generalize the reaction, waste refinery acid oil was esterified under the described reaction conditions. The conversion was estimated by acid-base titration technique. Further, the ester (EAE) was purified by percolation through basic alumina and analyzed by FTIR, ^{1}H, and ^{13}C NMR spectroscopic methods.

2.2.1 Epoxidation of 2-ethylhexyl oleate

A mixture containing 2-ethylhexyl oleate (5.6 g, 20 mmol) and formic acid (1.5 ml, 40 mmol) at 4 °C (ice bath) was added to an aqueous solution of 30 wt% H_2O_2 (6.25 ml, 80 mmol) dropwise, and the reaction was continued under vigorous stirring at room temperature for 5 h. After completion, the reaction mixture was washed with saturated $NaHCO_3$ solution and brine solution until neutralization was achieved. Furthermore, the organic layer was subjected to usual workup and concentrated under reduced pressure to give 2-ethylhexyl 9, 10-epoxy stearate (EPO) as a white product (4.8 g). The product was further confirmed by comparing its FTIR, ^{1}H, and ^{13}C NMR spectral data with authentic samples.

Under similar conditions, the 2-ethylhexyl ester of acid oil was epoxidized to the corresponding epoxide as a brownish product, EPA (9.0 g). The product was further confirmed by FTIR, ^{1}H, and ^{13}C NMR spectral analyses.

2.2.2 Synthesis of α-hydroxy ethers by oxirane ring opening

Oxirane ring opening was carried out by taking the epoxide of 2-ethylhexyl ester of acid oil (10 mmol) and octanol (10 mmol) as representative substrates under variable conditions, i.e., catalyst (0.5–5%), temperature 50–150 °C, and reaction time 1–6 h. After the reaction, the catalyst was recovered by simple filtration, and the residue obtained was washed with diethyl ether. The organic layer was dried and concentrated under reduced pressure. The product was further analyzed by ^{1}H NMR.

Furthermore, epoxide of 2-ethylhexyl fatty ester of acid oil was subjected to ring opening with different alcohols such as hexanol, decanol, 2-ethylhexanol, dodecanol, and glycerol under optimized experimental conditions. All the products were obtained in 85.5–96.5% yields.

2.2.3 Characterization of the products

Characterization of esters Fatty acid composition of the acid oil was found to be major component, $C_{18:1}$, and minor components, $C_{18:2}$, $C_{18:0}$, $C_{16:0}$, as determined by gas chromatography. FTIR, ^{1}H, and ^{13}C NMR data of 2-ethylhexyl oleate and 2-ethylhexyl ester of acid oil are summarized in Table 1.

In FTIR, the appearance of carbonyl band –C=O of ester at 1739 cm^{−1}, a multiplet at 1.2–1.3, 1.6 ppm related to the –CH_2, –CO–CH_2–CH_2 protons in ^{1}H NMR and peaks at 64, 173 ppm for –O–CH_2–, –COO in ^{13}C NMR, confirmed the successful formation of respective esters.
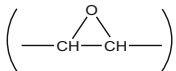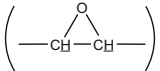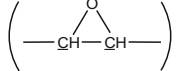
Characterization of epoxides The corresponding epoxides of 2-ethylhexyl oleate (EPO) and ester of 2-ethylhexyl acid oil (EPA) were confirmed by the disappearance of the signals corresponding to H–C= and –C=C– at 3008 cm^{−1}and 1514 cm^{−1}, respectively. Further, the appearance of a band at 1033 cm^{−1} due to oxirane ring formation confirmed the successful synthesis of corresponding epoxides. Also, in ^{1}H NMR spectra, the absence of peaks between 5.3 and 5.5 ppm due to the protons of –C=C– and new multiplet in between of 2.5 and 3.5 ppm due to the epoxide ring protons confirmed the formation of epoxide successfully.

Characterization of α-hydroxy ethers The epoxide of 2-ethylhexyl ester of acid oil (EPA) was subjected to oxirane ring-opening with different alcohols (hexanol, octanol, 2-ethylhexanol, decanol, dodecanol, glycerol) to give corresponding α-hydroxy ethers (ROP-1, ROP-2, ROP-3, ROP-4, ROP-5, ROP-6) as shown in Scheme 1. The spectral data (FTIR, ^{1}H, and ^{13}C NMR) of the products are summarized in Table 1. In the FT-IR spectra of the synthesized products, the characteristic bands appeared at 2926 and 2854 (–CH_2–); 1737 (C=O of ester); 1462 (–CH_2–); 1376 (–CH_3–); 1245, 1175, and 1096 cm^{−1} (ester C–O stretch); and additional peaks at 1145 (–C–OR–) and 3452 cm^{−1} (–OH). In ^{1}H NMR disappearance of peaks at δ 2.5–3.5 ppm and the emergence of new characteristics peaks in between 3.1–3.9 ppm and at 1.4–1.5 ppm due to -CH(OR′)-; -CH(OH)-; -OH and (–CH_2CH)OR′)–; –CH_2CH(OH)– respectively confirmed the formation of α-hydroxy ethers. The resonating signal at δ 73 ppm was assigned to the branching site (–CH(OR′)– and 83 ppm due to branching hydroxy group (–CH(OH)–) in ^{13}C NMR spectra.

3 Results and discussion

Acid oil, a waste residue achieved after the refining of the vegetable oil having FFA (149 mg KOH/g), has been used as a feedstock for the synthesis of lubricant range esters (α-hydroxy ethers) in the present study. The intended products were obtained by esterification, epoxidation, and finally ring opening of the oxirane ring. Initially, the reaction conditions were optimized by choosing oleic acid as a model substrate. Once the optimized reaction conditions were achieved, acid oil was treated under similar conditions. The esterification of oleic acid with 2-ethylhexanol was done using acidic 1,1,3,3-tetramethylguanidinium hydrogen sulfate (TMG.HSO_4) as a

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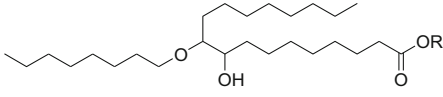**Table 1** IR, ^{1}H, and ^{13}C NMR characterization of esters, epoxides, and α-hydroxy ethers
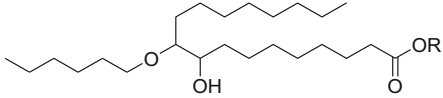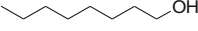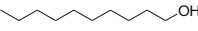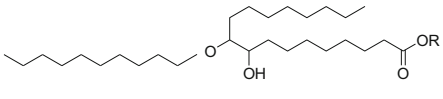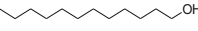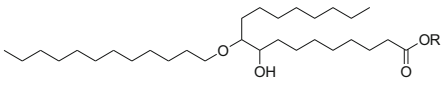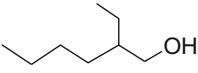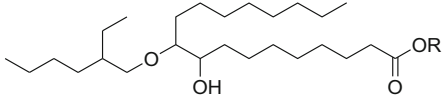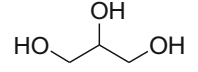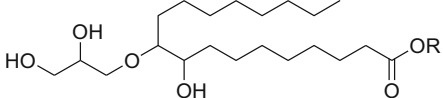
Substrates	IR cm^{-1}	^{1}H NMR (CDCl$_3$, δppm)	^{13}C NMR (CDCl$_3$, δppm)
Ester	2933 (C-H) 1739 (C=O) 1173 (C-C(=O)-O)	0.90 [t, (-CH$_3$)] 1.2-1.3 [m, (-CH$_2$)] 1.6 [m, (-CO-CH$_2$-CH$_2$)]	14.1 [2x(CH$_3$)] 22.7 [2x(CH$_2$-CH$_3$)] 32 [(C-C=C-C)] 34.3 [(C-CO)] 64 [(-O-CH$_2$-)] 130 [2 (C=C)] 173 [(-COO)]
Epoxide	1033.3 cm^{-1}	2.5-35	57.4, 57.1
α-hydroxy ethers	3452 cm^{-1} (-OH) 2926 and 2854 (-CH$_2$-) 1737 (C=O) 1462 (-CH$_2$-) 1376 (-CH$_3$-) 1245, 1175, and 1096 (ester C-O stretch) 1145 (-C-OR-) 724 (-CH$_2$-)	0.9 (3H, -CH$_3$) 1.3 (20H, -CH$_2$-) 1.4 (2H, -CH$_2$CH)OR')-) 1.5 (2H, -CH$_2$CH(OH)-) 1.6 (2H, -CH$_2$CH$_2$CO$_2$R) 2.3 (2H, -CH$_2$CO$_2$R) 3.1 (1H, -CH(OR')-) 3.6 (1H, -CH(OH)-) 3.9 (1H, -OH)	14 (-CH$_3$) 35 (-CH$_2$CO$_2$R) 73 (-CH(OR')-) 83 (-CH(OH)-) 174 (-CO$_2$R)

catalyst. The best conversion was obtained using a 5 wt% catalyst at 150 °C in 6 h as described in the "Experimental section." Further esterification of the acid oil was performed with 2-ethylhexanol under the optimized reaction conditions to yield corresponding 2-ethylhexyl ester of acid oil. Subsequently, 2-ethylhexyl ester of oleic acid and acid oil was subjected to epoxidation using performic acid (HCOOH/H$_2$O$_2$), and then oxirane ring was opened with different alcohols in the presence of P–C–SO$_3$H acid catalyst to afford desired α-hydroxy ethers.

3.1 Effect of reaction parameters on oxirane ring opening

At first, the effect of catalyst loading, reaction temperature, and reaction time was evaluated on the epoxide of 2-ethylhexyl ester of acid oil with 1-octanol. The results obtained by varying the reaction temperature from 50 to 150 °C are summarized in Fig. S4. As shown, the best conversion (96.83%) was achieved at 100 °C. Further enhancement in temperature did not make a significant

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Table 2 P–C–SO$_3$H-catalyzed ring opening of epoxide of 2-ethyl hexyl ester of acid oil with different alcohols

Entry	Reactant	Alcohol	Product	[a,b]Conv./[c]Yield (%)
1	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			94.2/90
2.	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			96.6/95
3.	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			97.4/88
4.	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			93.5/ 91
5.	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			91.6/91
6.	Epoxide of 2-ethyl hexyl ester of acid oil (Acid oil composition: (Major component-C18:1; Minor component- C18:2, C18:0, C16:0))			93.8/86

Reaction condition: 2-ethyl hexyl ester of acid oil (10 mmol), alcohol (10 mmol), catalyst P–C–SO$_3$H 2 wt%, reaction time 5 h, temperature 100 °C

[a] Determined by ^{1}H NMR integration method, over the signals representing the reactant and products

[b] In all cases selective formation of the given product obtained without any by-product formation

[c] Isolated yield: (actual yield/theoretical yield) × 100%

difference in the conversion. Next, the reaction was studied by varying the catalyst concentration from 0.5 to 5 wt% (P–C–SO$_3$H) at 100 °C for 5 h (Fig. S5). The maximum 96% conversion was achieved when 2 wt% of the catalyst was utilized. Further, the reaction was found to be affected adversely with increasing the catalyst concentration beyond 2 wt%, which is most likely due to the possibility of the formation of by-products under highly acidic conditions.

Furthermore, the effect of reaction time was evaluated by withdrawing the samples after a definite period and measured by ^{1}H NMR spectroscopy. The reaction was found to be very fast in the beginning and gave about 61% conversion in 1 h. However, as the reaction proceeds, a marginal increment in the reaction rate was observed, and the maximum 96% conversion was achieved in 5 h (Fig. S6). Next, the reaction was generalized by using different linear and branched alcohols such as hexanol, decanol, 2-ethylhexanol, dodecanol, and

Fig. 1 Recycling of P–C–SO$_3$H for the oxirane ring opening
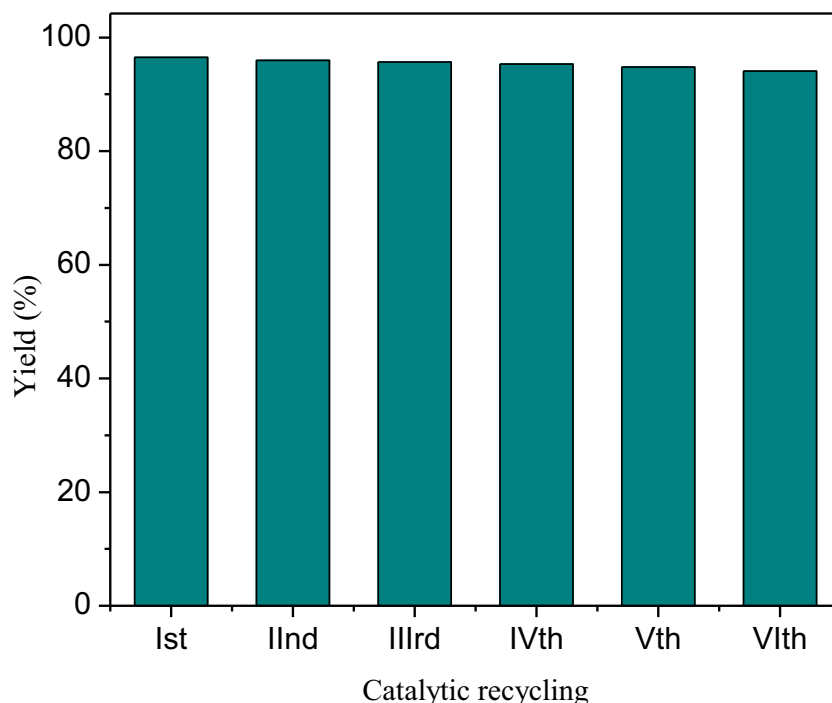
glycerol under optimized experimental conditions. The results of these experiments are summarized in Table 2. As can be seen from Table 2, all the epoxides were efficiently converted and afforded high to the excellent yield of the α-hydroxy ethers in 86–97%.

Furthermore, the recyclability and reusability of the catalyst were checked for the ring opening of epoxide of 2-ethylhexyl oleate with 1-octanol under described reaction conditions. The catalyst could easily be recovered by simple decantation, washed with methanol, and dried at 80 °C for 4–5 h before recycling run. The recovered catalyst was reused for

the subsequent six runs using fresh substrates under optimized conditions. The results of these are mentioned in Fig. 1. As can be seen in results, the catalyst exhibited consistent activity, and no leaching of sulfonic acid groups was observed during reactions. In order to confirm the leach-proof nature of the catalyst, we measured the sulfur content of the used catalyst that was recovered after the sixth recycling run. The value of sulfur content in the recovered catalyst was found to be 2.43 mmol H$^+$ per g as determined by elemental analysis assuming that all the sulfur atoms are presented in –SO$_3$H form. This value is almost similar to the fresh one (2.44 mmol

Table 3 Physicochemical characteristics of substrates, their epoxides, and α-hydroxy ethers

S. No.	Substrates/products	Density (g/cm^3)	Pour point (°C)	Viscosity (cSt)		Viscosity index
				At 40 °C	At 100 °C	
1	Oleic acid	0.9002	+ 6	22.67	4.99	153
2	Acid oil	0.9245	− 9	46.18	8.44	161
3	ESE	0.8643	− 30	9.24	2.82	168
4	EAE	0.8900	− 15	20.97	4.27	184
5	EPO	0.9060	− 15	14.03	3.52	135
6	EPA	0.9433	− 12	46.85	7.86	137
7	ROP-1	0.9419	− 6	48.56	7.50	119
8	ROP-2	0.9253	− 9	25.46	4.30	73
9	ROP-3	0.9357	< − 27	52.93	7.31	97
10	ROP-4	0.9371	− 15	73.0	9.11	99
11	ROP-5	0.9152	< − 27	42.57	7.48	143
12	ROP-6	0.9616	− 6	140.90	11.24	48

H^{+} per g), which evidently suggests that the catalyst is quite stable and truly heterogeneous in nature without showing any detectable leaching of –SO$_3$H groups.

3.2 Evaluation of physicochemical properties of synthesized products

The reactants oleic acid and acid oil (**1–2**); their esters ESE and EAE (**3–4**); epoxides EPO and EPA (**5–6**); and their α-hydroxy ethers ROP-1, ROP-2, ROP-3, ROP-4, ROP-5, and ROP-6 (**7–12**) were evaluated for physicochemical properties such as viscosity at 40 and 100 °C, density, viscosity index, and pour point as shown in Table 3.

The pour point of the oleic acid and acid oil was improved after esterification in ESE and EAE (Table 3, entries 3–4) due to the addition of 2-ethyl hexyl ester moiety. The pour point of oleic acid and acid oil was determined as + 6.0 °C and − 9 °C, respectively. The chemical structure of the oleic acid is not so linear and has some steric hindrance due to an unsaturation between C-9 and C-10 cis conformation, which breaks the linearity of the molecule. But, it is not sufficient to overcome the intermolecular interaction forces due to hydrogen bonding between the molecules. After esterification of oleic acid and acid oil, the pour point value decreases to − 15 and − 30 °C, respectively. The addition of branched-chain alcohol (2-ethylhexanol) after esterification increases the effective steric hindrance of the molecule and considerably reduces the pour point as compared with their fatty acids. Thus, after the esterification, the reduction in intermolecular interactions due to the lack of hydrogen bonding reduces the flow behavior of the esters. The study is comparable with J.P.C. Marques et al. [26]. The pour point was further increased in epoxidized products (EPO and EPA). This is due to the intermolecular interactions after the oxirane ring formation, whereas a significant variation was observed in corresponding α-hydroxy ethers, as shown in Table 3, entries 7–12. As anticipated, the chain length of the alcohol improved the pour point of the product, which can be assumed due to the effective formation of highly disorder macrocrystalline structures with higher alkyl chain length at reduced temperatures. Among all the α-hydroxy ethers formed, ROP-3 and ROP-5 (< − 27 °C) exhibited best results which are probably due to the branched and long-chain structure of the corresponding alcohols (Table 3, entry 9 and 11).

Besides this, insertion of α-hydroxy ether moiety at the mid-chain in the structure not only influences the pour point but also increases their viscosity at 40 °C. After the oxirane ring-opening reaction, the formation of one free hydroxyl group provides intermolecular hydrogen bonding interactions between the molecules. As shown in Table 3, the viscosity of synthesized esters of oleic acid and acid oil (entries 3–4) became lower as compared with their corresponding acids (entry 1, 2); however, after epoxidation, a remarkable enhancement in the viscosity was observed (Table 3, entries 5–6). The viscosity of synthesized α-hydroxy ethers (ROP-1 to ROP-6) at 40 °C and 100 °C was found to be significantly increased than their epoxide counterparts. This enhancement in viscosity is presumed due to the higher molecular weight and stronger intermolecular interactions resulting from the branching at the middle of the product molecule [27]. A significant decrease in pour point (< − 27 °C) was observed in the case of ROP-5 due to enhancement of steric hindrance at mid-point by the addition of branched chain moiety. Furthermore, a dramatic improvement in viscosity, 140.90 at 40 °C, was observed (Table 3, entry 12) when glycerol, a highly viscous alcohol, was used for the ring opening. The presence of three hydroxyl group (one hydroxyl group (–OH) in the main chain and other two free hydroxyl group of glycerol moiety) provides strong intermolecular hydrogen bonding, which led to a very high viscosity [28]. Viscosity index (VI) is defined as the change of viscosity with variations in temperature. The viscosity index of esters ESE and EAE was found to be higher 168.02 and 184.29, respectively, as compared with their corresponding acids 153 and 161.21. The epoxidation of the esters lowers the VI. Further, VI decreases for α-hydroxy ether derivatives after oxirane ring opening due to the reduced linearity of the molecule by the branching in the mid-chain. In ROP-6, a significant decrease in VI, i.e., 48, was observed due to the insertion of the glycerol molecule.

4 Conclusion

We have described the synthesis of various bio-lubricant esters from epoxide of 2-ethylhexyl ester of acid oil by ring opening with different alcohols using polymer-grafted sulfonated carbon composite (P–C–SO$_3$H) as a heterogeneous acid catalyst. The use of heterogeneous catalyst offers several advantages such as secure handling, higher thermal stability, and efficient recovery and recycling as compared with the commonly used catalysts such as p-toluene sulfonic acid. A series of α-hydroxy ethers were synthesized using different alcohols by following esterification and epoxidation steps. A systematic study of the variation in pour point, viscosity, and viscosity index with different modifications introduced due to the various alcohols used for ring opening was performed. The difference of the polarities and symmetry of the synthesized samples were responsible for the significant differences in the physicochemical properties. Among the all, two products ROP-3 and ROP-5 exhibited best results as < − 27 °C pour point (PP) and viscosity index (VI) 97 and 143, respectively. The insertion of chain at the mid-point creates the steric hindrance in the molecules, which generate sufficient repulsion to better overcome the higher interaction forces. High VI and a lower pour point indicate ROP-3 and ROP-5 to be the most promising as bio-lubricant, thus enabling applications at lower temperatures.

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