Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Synthesis and Evaluation of Polymeric Dispersant Based on Vegetable Oils Their Application as Cutting Fluid

Nasser R. Abd El-Rahman*, **Mahmoud Bekhit, Nabel A. Negm and Zizi I Abdeen**

Petrochemicals Department, Egyptian Petroleum Research Institute, Cairo, 11727 Egypt

Abstract

In this work, a novel vegetable oil-based polymeric agents were prepared by epoxidation of rapeseed oil (RO) and castor oil (CO) followed by ring opening reaction of epoxidized products, (epoxidized rapeseed oil and epoxidized castor oil) (ERO) and (ECO) with polyethylene glycol with different molecular weights (400, 600 and 10000 g/mole). The prepared polymers were characterized by ^{1}H NMR, FTIR and GPC for determination of molecular weight. The properties of epoxidized vegetable oil (EVO) and Polymeric vegetable oils (polymeric dispersant of rapseed (PDR) and (polymeric dispersant of castor (PDC) were studied. The prepared polymers were employed as emulsifiers for metal working cutting fluids (MWCF) application.

Keywords: Vegetable oils; Epoxidized vegetable oils; Polymeric dispersant; metal working fluids; Rapeseed; Castor oil.

1. Introduction

Vegetable based oils are more potential candidates for the use in industry as lubricants/MWFs. Several studies are in growth to develop new bio based cutting fluids based on various vegetable oils available around the world. In this article to review the literature on various potential vegetable oils being developed as metal working fluids by different authors. Further, their theoretical and experimental results obtained are reported. Vegetable oils are a part of great family of chemical compounds known as fats or lipids which made up mainly of tri esters of glycerol with fatty acids which can be achieved into high value oleo chemicals for various industries [1, 2].The fatty acids of vegetable oils may be saturated and unsaturated fatty acids. Castor oil, cottonseed oil, linseed oil, Jatropha oil, rapeseed oil and soybean oil are examples on vegetable oils [3,4]. The unsaturation present (double bond) in vegetable oils can be chemically improved to form epoxidized vegetable oils [5, 6]. Epoxidation of double bond has been studied in many papers [7, 8]. Epoxidation is commonly performed using organic peracids formed in situ via the attack of H2O2 on a carboxylic acid in aqueous solution [9]. Due to the high reactivity of the oxirane ring, epoxides can also be used for the synthesis of chemicals like olefinic, carbonyl compounds, alcohols, alkanol amines, glycols and polymers like polyurethanes, epoxy resin, polyesters [10,11].Since vegetable oils are ecofriendly, sustainable and renewable; both castor oil and Rapeseed oil were the target of this work. Castor oil is obtained from the seeds of the castor oil plant ricinus. It contains of about 90% Ricin oleic acid (12-hydroxy-cis-9-octodecenoicacid) which makes it a very suitable for industrial purpose like cosmetics, paints, adhesives, plastics, rubbers, and pharmaceuticals [12,13]. Likewise, the major fatty acid in its chemical structure is linoleic acid. Thus these oils were greatly used in versatile industrial fields including: coatings, printing inks, adhesives, lubricants and plastics [14,15]. Among the various reactions of oxirane aminolysis is a classical route to β-amino alcohols formation, an important class of compounds with pharmaceutical and biological properties [16]. Various compounds were prepared by the aminolysis of epoxides with amines under basic or acidic catalysts in organic solvents[17, 18].The chemical structure of Polyethylene glycol, we report the synthesis of ecofriendly polymeric dispersant for metal working cutting fluids application by epoxidation of rapeseed oil, Castor oil followed by ring opening using polyether amine and poly propylene glycol[19]. Lubricants are being used

in all divisions of industry for lubricating their machines and materials. Reports designate that nearly 38 million metric tons of lubricants were used globally in 2005, with an expected increase of 1.2% over the next decade[20].About 85% of lubricants being used everywhere the world are petroleum-based oils[21]. Huge use of petroleum based oils, created several harmful effects on environment. The major harmful effect is mostly linked to their inappropriate use, which results in surface water and groundwater pollution, air contamination, soil pollution, and so, agricultural product and food pollution[22].Metal working fluids are one of the types of lubricants, which are widely used in machining operations. There are many types of metalworking fluids (MWFs), which may be used to do such tasks [23]. Maximum of the MWFs are mineral oil based fluids. These fluids increase productivity and the quality of manufacturing operations by cooling and lubricating during metal forming and cutting operation[24]. Due to their advantages, the feeding of MWFs is increasing in machining industry. It is educated that European Union alone uses about 320,000 tons per year of MWFs of which, at least two-thirds need to be disposed[25].In spite of their public use, they pose important health and environmental hazards through their life cycle. It is reported that about 80% of all professional diseases of operatives were due to skin contact with cutting fluids[26,27]. Evaluation says that in USA alone about 700,000 to one million workers are exposed to MWFs [28]. As cutting fluids are complex in their conformation, they may be irritant or allergic. Even microbial toxins are generated by bacteria and fungi current, mainly in water-soluble cutting fluids[29].Which are more dangerous to the operators. To overcome these challenges, various alternatives to petroleum-based MWFs are currently being explored by scientists and tribologists. Such alternatives include synthetic lubricants, solid lubricants and vegetable-based lubricants. In general, vegetable oils are highly attractive substitutes for petroleum-based oils because they are environmentally friendly, renewable, less toxic and readily biodegradable[30, 31].
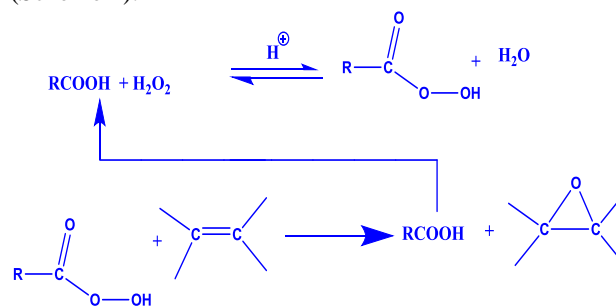
2. Experimental

2.1. Materials

Chemicals were obtained as follows: Castor oil (CO), rapeseed oil (RO), polyethylene glycol (Invista Specialty Chemicals), and ethyl acetate and methanol (Petrochem-KSA), hydrogen peroxide 50% (Piochem), zinc chloride, magnesium sulfate and p-toluene sulfonic acid (Oxford), formic acid, glacial acetic acid, sodium chloride, sodium carbonate (ADWIC-Egypt).

2.2. Preparation of polymeric Dispersants

2.2.1. Epoxidation of vegetable oils

For epoxidation of castor oil (50 g) and acetic acid (11.4 mL)[32], in case of rapeseed oil (50 g) and formic acid (15 mL). Oil and acid were mixed in a round bottom flask and stirred at 550 rpm under controlled temperature through using a water bath at a temperature of 50±2 oC. To start the epoxidation, hydrogen peroxide 50% solution (26.4 mL) was added drop wisely into the reaction mixture during the first 2 h of the reaction. The molar ratio of the double bonds in the reacted oils (obtained from iodine value of the oil) to hydrogen peroxide (C=C: H_2O_2) was 1:1.7. After the charging of H_2O_2 was completed, the reaction continued under mixing and controlling the temperature at 50 oC for a further 5 hours then the mixture was cooled to room temperature, To purify the epoxidized oil, it was poured into a 500 mL separating funnel and the oil layer was washed successively with 5% sodium carbonate solution (50 mL) and 5% sodium chloride solution (50 mL), respectively. Ethyl acetate (50 mL) was added to enhance the separation of the oily product from the water phase. The water and solvent were then distilled off under a rotary vacuum evaporator; the oil phase was further dried above anhydrous magnesium sulfate and then filtered, (Scheme 1).

Scheme 1: Reactions of epoxidation of oils with peracids formed in mixture

A series of polymeric dispersants were prepared based on two different types of epoxidized vegetable oils (Epoxidized rapeseed oil and Epoxidized Castor oil) by conventional epoxidation method followed by ring opening using polyethylene glycol with different molecular weight.

2.2.2. Preparation of polymeric dispersant 1 (PD-R)

PD- R was prepared by ring opening of epoxidized rapeseed oil (20 g) using polyethylene glycol (400, 600 and10000 g/mole) (40 g), where epoxidized rapeseed oil and polyethylene glycol were mixed in 250 mL round bottom flask in the presence of p-toluene sulfonic acid as a catalyst at a temperature of 110o C for 8 h; ethyl acetate (100 mL) was added to the reaction mixture as a solvent[33]. The prepared polymer was filtered and washed by water to remove the catalyst. The excess water and ethyl acetate was distilled by vacuum distillation to obtain product of approximately100% solid content see Scheme 2.

2.2.3. Preparation of polymeric dispersant 2 (PD-C)

PD-C was prepared by ring opening of epoxidized castor oil (ECO) where ECO (20 g) was mixed with Polyethylene glycol (400, 600 and10000 g/mole) (40 g) in 250 mL round bottom flask in the presence of $ZnCl_2$ as a catalyst at 60–70o C for 4 h. Ethyl acetate (100 mL) was added to the reaction mixture as a solvent[34]. The prepared polymer was purified by filtration of solid catalyst, and the excess ethyl acetate was distilled using vacuum distillation to obtain a product of approximately 100% solid content see Scheme 3.

2.3. Formulation of cutting fluids

The prepared additives (2 gm) were used as emulsifiers in the formulation of the cutting fluids in the following composition: 20 mL distilled water, 5 mL of natural oil (Waste cooking oil, Castor oil, Rapeseed and Coconut), and second formulation is 20 mL of natural oil (Waste cooking oil, Castor oil, Rapeseed and Coconut) (0.5 gm) were used as emulsifiers in 5 mL distilled water. The mixture was mixed in high speed mixer (5000 rpm) for15 minutes at 25oC[35].

2.5. Evaluation of Metal Cutting Fluids Additives

2.5.1 Emulsion Stability

It describes the stability of the metal cutting fluids formulations and their ability to be homogeneous during storage, transportation and application [36]. The metal cutting fluid formulations which formulated in the presence of the synthesized additives were placed in graduated cylinders at 25 oC and the appearance of oil layer in each cylinder was monitored during 14 days in term of oil layer volume in mL. The emulsion stability (%) was calculated in percent according to the following equation:

$$\text{Emulsion Stability \%} = (1 - \frac{V2}{V1}) \times 100$$

Where V1 = Volume of oil separated

V2 = Volume of oil in emulsion

2.5.2 Kinematic Viscosity at 40 ºC and 100 ºC

It defines the viscosity of the cutting fluid formulation at 40 ºC which is appropriate for metal working at low temperatures of bending and twisting and at 100 ºC which is suitable for metal working at high temperatures of cutting and welding[37]. The measurements were done using Ubelhood suspended level viscometer with a capillary diameter of 0.3 mm for measurements at 40 ºC, and a capillary diameter of 0.1 mm for measurements at 100 ºC.

2.5.3 Antirust Test

The protection of the metal throughout the handing out in the presence of the cutting fluid formulations was tested by copper strip test according to the standard method[38]. A copper strip was immersed in the different formulated metal cutting fluids (300 mL) at 25 oC in three replicates for 24 h and the test strip is observed for signs of rusting and the degree of rusting. The rusting degree was considered in a scale from 0 to 10. No rust was 10 degree and completely rusted was 0 degree.

2.5.4 Specific Gravity

It defines the workability of the cutting fluid formulation during the processing of metal fabrics. The measurements were made using (specific gravity flask) of 25 mL. An empty flask was weighted accurately, and then it was occupied with the metal cutting fluid formulation, and weighted. Test was recurrent three times at 25 oC, and the average was considered[39]. The difference in the weight was used to calculate the specific gravities of the metal cutting fluids according to the following equation:

$$\text{Specific Gravity} \frac{W2 - W1}{V}$$

Where W1 = weight of empty flask
W2 = weight of filled flask
V = volume of flask

2.5.5 Surface tension

It defines the surface spreading of the metal cutting fluids formulations on the metal surface in term of surface tension value. Surface tension data (γ) of the different formulations were measured by Du-Noüy tensiometer (Krüss type K6) (Hamburg, Germany) using platinum ring detachment method. The tensiometer was calibrated by deionized water at 25

°C. The surface tension measurements were taken after 10 min. of pouring the solution in the measuring cup to ensure the equilibrium[40].

2.5.6 pH values

It defines the acidity or alkalinity of the metal cutting fluids formulations and their tendency to cause rust or corrosion for the metal surface. The values of pH were reported using a pH meter for the different formulated metal cutting fluids at 25 °C after 1 day of formulation.

3. Results and discussion

3.1. Characterization of the polymeric dispersants and intermediates

The reaction between the oils and the hydrogen peroxide involves formation of oxirane ring as a result of the reaction between the double bonds and the active oxygen in a neucleophilic attack reaction, Scheme 1. The formation of the products proceeded by the ring opening of the oxirane ring via hydrolysis reaction to obtain the two products represented in Schem2 and Scheme 3.

3.1.a FTIR spectra

Figure 1 shows the disappearance of the absorption bands of C=C-stretch at 3009 cm-1 in the fatty acids moieties, which demonstrates the conversion of the double bond of the oils to the epoxy group during the epoxidation reaction to obtain epoxidized rapeseed oil (ERO) and epoxidized castor oil (ECO). The formation of the epoxy groups in the oil molecules was indicated by the appearance of absorption bands at 843 and 824 cm-1. The groups which did not incorporate in the epoxidation reaction were: C=O ester groups and the hydroxyl groups of the triglycerides which present at 1743 and 3460 cm-1, respectively.
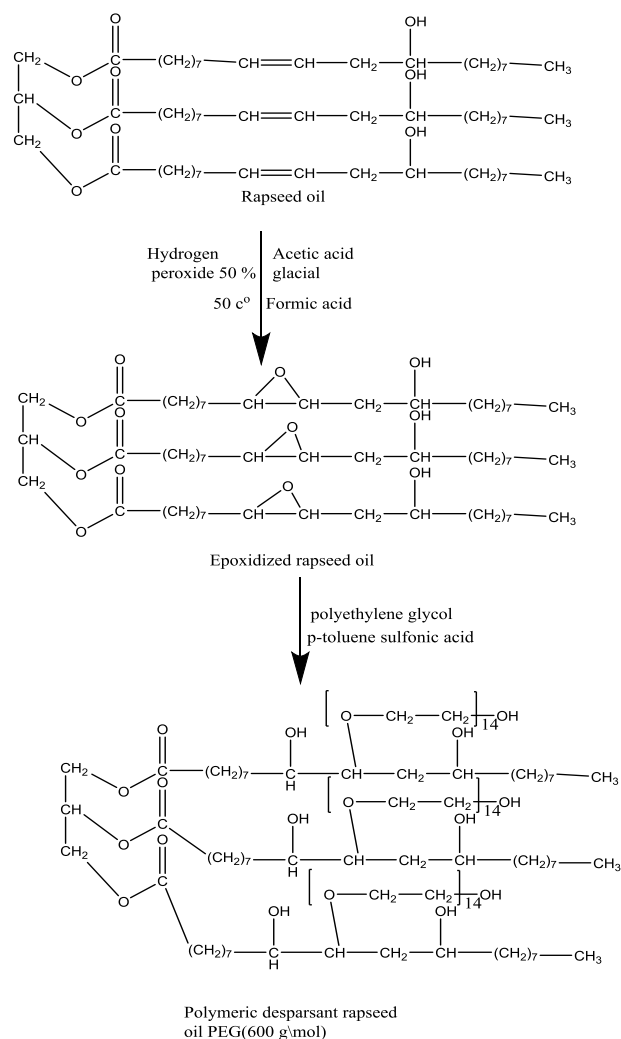
FTIR spectra of the prepared polymeric dispersants (PD-R-PD-C) were represented in Figure 1. it is clear in Figure 2 the appearance of the characteristic bands of poly ethylene glycol : at 2740 cm−1 and 2888 cm−1 for symmetric and asymmetric stretching vibrations of C-H groups, respectively; 1469 cm−1 and 1345 cm−1 assigned for the bending vibrations of C-H groups, respectively; 1060 cm−1 assigned for ether C–O–C band of poly ethylene glycol; 1743 cm–1 assigned for stretching of C=O ester groups of the triglyceride; and a signal at 3458 cm−1 assigned for the stretching vibration of the hydroxyl group, OH).
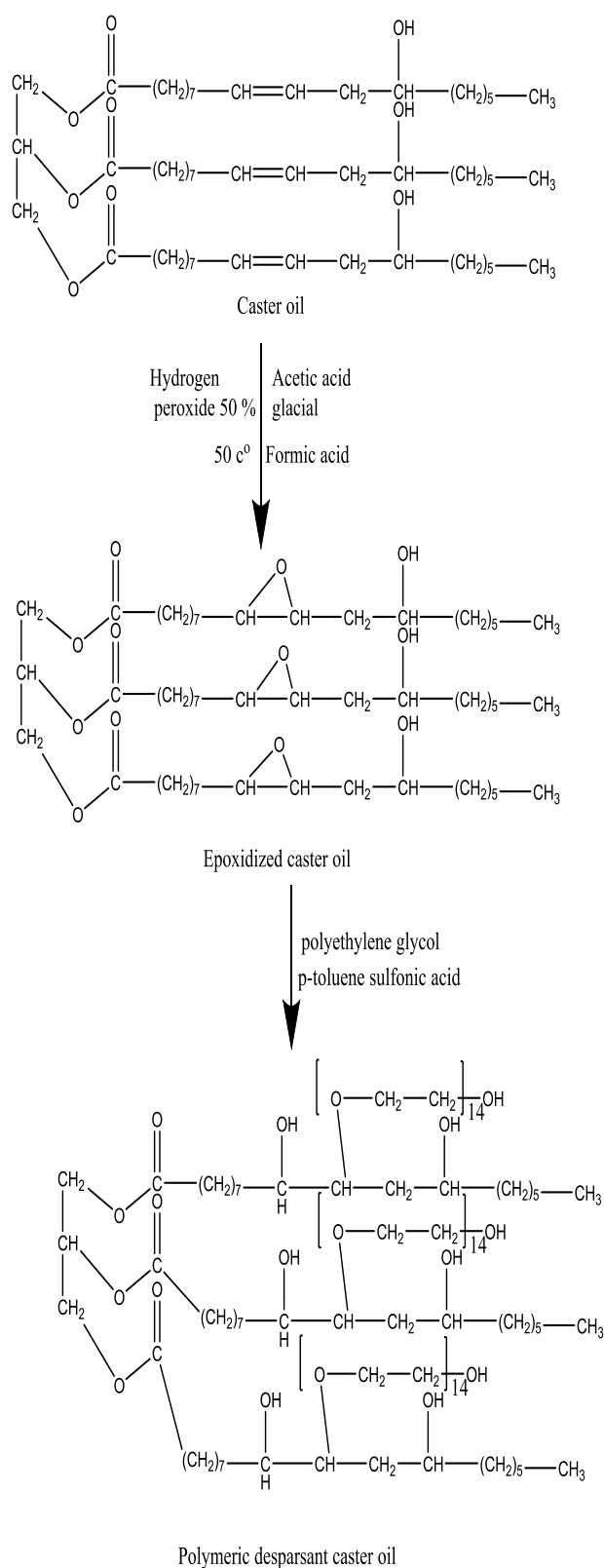
3.1. b 1H NMR spectra

The chemical structure for the prepared compounds that identified by 1H NMR spectroscopy shown a peak at δ = 0.842 ppm (t, CH3-(CH2)7 –CH-OH), δ =

1.18 ppm (m, CH3- CH2 (CH2)6 –CH-OH), δ = 1.24 ppm (m, CH3- (CH2)6- CH2 –CH-OH), δ = 3.439 ppm (m, CH3- (CH2)6- CH2 –CH-OH), δ = 4.0625 ppm (d, CH3- (CH2)6- CH2 –CH-OH), δ = 2.50 ppm (d, -CH2-CHOCH-CH2) Oxiran see Figure 3: The 1H NMR spectra of epoxidized rapeseed oil.

- shown a peak at δ = 0.85 ppm (t, CH3-(CH2)7 –CH-OH), δ = 1.1819 ppm (m, CH3- CH2 (CH2)6 –CH-OH), δ = 1.51 ppm (m, CH3- (CH2)6- CH2 –CH-OH), δ = 3.485 ppm (m, CH3- (CH2)6- CH2 –CH-OH), δ = 4.556 ppm (d, CH3- (CH2)6- CH2 –CH-OH), δ = 5.32 ppm (d, O-CO-(CH2)7 –CH-OH), δ = 5.3514 ppm (t, O-(CH2 –CH2)14-OH) in polyethylene glycol and δ = 11.99 ppm (CH3COOH, Excess of acid) ; see Figure 5: The 1 H NMR spectra of polymeric dispersant 600 for rapeseed oil

Scheme 2: Chemical structures of the prepared dispersants rapeseed (polyethylene glycol 600(400 and 10000g\mol)

Caster oil

Hydrogen peroxide 50 % | Acetic acid glacial

50 c° | Formic acid

Epoxidized caster oil

polyethylene glycol
p-toluene sulfonic acid

Polymeric desparsant caster oil

Scheme 3: Chemical structures of the prepared dispersants castor oil (polyethylene glycol 600 g\mol (400 and 10000g\mol)

3.1. c Molecular weights determination

The molecular weights were determined using GPC Agilent model 1515 pump system equipped with 1260 infinity refractive index detector and using THF as eluent, operating with a flow rate of 1.00 mL/min at 35o C. Column PL-gel 3 lm Mixed E 300 7.5 mm covering a molecular weight range of 600–400 and10000 mg/g was used and was calibrated using polystyrene standards. The molecular weights of the prepared compounds and their starting materials (as they are obtained from the local market) were determined in terms of the number average molecular weight (Mn) and molecular weight polydispersity index (PDI) using Gel Permeation chromatography (GPC), Table 1

Table 1: Gel permeation chromatographic data of the prepared polymeric dispersant

Sample	Mn	Mw	PDI
STD	2386.7	4978.5	1.28
Rapeseed oil	1267.3	1329.2	1.04
Castor oil	1109.8	1054.3	1.05
PD-R1	1403.5	1442.1	1.20
PD-R2	1687.2	1710.5	1.12
PD-R3	10169.2	11414.5	1.31
PD-C1	1430.1	1510.4	1.42
PD-C2	1640.5	1715.7	1.25
PD-C3	10080.3	11170.3	1.16

Data in Table 1 showed that the formation of the different polymeric dispersants

3.2 Evaluation of the metal cutting fluids formulations

3.2 .1 Rust Inhibition Properties

The capability to provide corrosion protection is significant for a metalworking fluid. The emulsions were assessed for rust formation on copper. Table 2& Table 3 represent the results of the antirust test before and after synthesized additive added to the formulation after 1 and 10 days of immersion. The rust is formed on the metal surface during its processing due to its interaction by water and atmospheric oxygen. One role of metal cutting fluid is avoiding the rust formation on the metal surface during metal handing out[41]. The origin of antirust formation in the presence of the formulated metal cutting fluid is the presence of two effective moieties in the chemical structure of the synthesized additives. The first is the alkyl moieties of oleic, linoleic or

fatty acid mixture obtained from oil hydrolysis. Saturated and unsaturated fatty acids were reported as efficient additives for rust prevention in cutting fluids formulations[42]. Unsaturated fatty acids including oleic acid, linoleic, recinoleic and maleic acids were incorporated in cutting fluid formulations as anticorrosion additives and showed excellent anticorrosion test results in presence copper and iron metals[43]. The second is the polyethylene glycol chains in the chemical structure of the synthesized additives, which increases the adsorption of the additives on the metal surface. That protects the metal surface from the influence of corrosive compounds [44]. The obtained rust test results listed in Table 1 show two behaviors. After one day immersion in the metal cutting fluid, the copper surface showed no corrosion effect on the surface; 10 unit on anticorrosion scale. The results of antirust after one day immersion show high protective tendency of the formed emulsion. After ten day immersion of copper strips in the formulated metal cutting fluids, the antirust scale was ranged between 6 and 8. These results display high antirust efficiency of the different formulations. The emulsions studied showed excellent antirust properties after 10 days. The modified formulations contain hydroxyl and long chain alkyl chains, which may be responsible for the rust inhibition[45]. It can conclude that this cutting fluid has good ability to inhibit the corrosion.

3.2.2 Kinematic viscosity

Viscosity is an important property with respect to fluid performance and maintenance. Lower viscosity fluids allow grit and dirt to settle out of suspension. Removal of these contaminants improves the quality of the fluid recirculating through the machining system. This can impact product quality, fluid life and machine shop productivity. Kinematic viscosity represents the viscosity of the cutting fluid formulation used at the metal surface. Viscous metal cutting fluids are favorable in the machining processes. The high viscosity of vegetable oils gives the cutting fluid an oily aspect and good lubricating properties. At certain viscosity, the increase will decrease the efficiency of the metal cutting fluids due to the loss of fluidity and consequently the lubricity power of the fluid decreases. Kinematic viscosities at 40 oC of castor oil are 293.4 cSt respectively[46]. The kinematic viscosity of the metal cutting fluids formulations depend on molecular weight of PEG as can be seen from the data listed in Table 2& Table 3. The solubility of PD were by increase number of ether bond increase solubility of PD as metal cutting fluid and thus, decrease the viscosity as seen from table 1 the viscosity of PD3-R10000PEG With Castor at 40oc are 149 cSt Viscosity of formulated cutting fluid decrease by decrease viscosity of oil used in formulation viscosity of PD3-R10000PEG With coconut at 40oc are 5.4 cSt.

3.2 .3 Emulsion stability

Metal cutting fluid formulation is simply emulsions of oil in water. The stability of that emulsion is a key phenomenon which determined the applicability of the cutting fluid in metal processing [47]. The emulsification power determines the stability of the cutting fluid after certain time. Decreasing the emulsion stability of the metal cutting fluid leads to the separation of oil phase from aqueous phase to form two layers. Generally, the formulated cutting fluids with the synthesized additives showed stable emulsions up to 30 days, Table 2& Table 3. Furthermore, the stability of emulsions formed depends mainly on the oil type and fatty acid residue linked to PD. In case of PD3-R10000PEG, the stabilities of the emulsions formed from Rapeseed oil were comparatively high compared to emulsion formed from water. That can be attributed to the high percentage of Erucic acid (22:1) 54.0 % content in the chemical structure of the Rapeseed oil. From the results of emulsification tendency of the synthesized emulsifiers, once can be conclude that the emulsifiers of oils in metalworking fluids are specific chemicals, and their stability depends on their compatibility with the used oil.

3.2 .4 Surface tension
Cutting fluids perform their action between the metal surface and fabricating tools. The distribution of the cutting fluid on the metal surface depends on the contact between the liquid and the metal, i.e., surface or interfacial tension. Decreasing the surface tension of the cutting fluid formulations increases their distribution on the surface. The surface tension values of the formulated cutting fluids by the synthesized additives as emulsifiers are ranged between 35 and 41 mN/m. The obtained values are considered low values, which provide high contact and spreading on the metal surface. Commercial cutting fluids containing different fatty acids provided comparatively higher surface tension values ranged between 39 and 58 mN/m [48].

3.2 .5 pH values
Acidity or alkalinity of metal processing medium is a strong reason for metal corrosion. Reserving the medium at neutral pH protects the metal against corrosion (especially copper and aluminum)[49]. The pH values of the prepared formulations are ranging between 3.4 and 5.1 after 7 days, Table 2& Table 3. These values don't change by time, indicating the chemical stability of the different formulations. The

derivatives are esters formed between different fatty acids and glycolyzed polyurethane. Hydrolysis of the ester additives as metal cutting fluids formulations can be occurred. The risk of esters hydrolysis is found in alkaline medium (at higher pH values than 8) and also in slightly acidic medium (at lower pH values than 6).

3.2 .6 Specific Gravity

The specific gravity of the different metal cutting fluids formulations are ranging between 0.897 g/mL and 0.958 g/mL at 25 oC, Table 2& Table 3. The obtained values are comparable to the specific gravity of water[50].

4. Conclusions

From the results of the study several concluding points can be extracted:
1- The prepared polymeric as expected compound from characterized for structure
2- The prepared additives have high emulsification power and produce stable oil in water emulsions, compared to the commercial and recently synthesized nonionic Sorbian, polyethylene glycol and glycerol based emulsifiers.
3- The anticorrosion behavior of the formed emulsions is very high, and reached to 30 days, which is comparatively high efficiency.
4- The spreading power of the emulsions made by the prepared additives is high compared to the nonionic additives.
5- The acidity of the emulsions formed is in an acceptable range of 6 to 7.
6- The efficiencies of the formulations formed by the synthesized additives are comparatively higher than the formulations contained nonionic surfactants and modified vegetable oils.
7- The emulsifiers are specific for the oil used in metal working fluid formulation and can be prepared from the hydrolyzed fatty acids of the oil incorporated in the formulation.

5. Conflicts of interest

All authors have participated in writing this manuscript, this manuscript has not been submitted to or under review at another journal or other publishing vein.

6. Acknowledgments

7. References

1. Milchert, E., K. Malarczyk-Matusiak, and M. Musik, Technological aspects of vegetable oils epoxidation in the presence of ion exchange resins: a review. Polish Journal of Chemical Technology, 2016. 18(3).
2. Mudhaffar, B. and J. Salimon, Epoxidation of vegetable oils and fatty acids: catalysts, methods and advantages. Journal of Applied Sciences, 2010. 10(15): p. 1545-1553.
3. Yossif, N.A., et al., Preparation and characterization of polymeric dispersants based on vegetable oils for printing ink application. Progress in Organic Coatings, 2017. 111: p. 354-360.
4. Vlček, T. and Z.S. Petrović, Optimization of the chemoenzymatic epoxidation of soybean oil. Journal of the American Oil Chemists' Society, 2006. 83(3): p. 247-252.
5. Zhan, G., et al., A novel biobased resin-epoxidized soybean oil modified cyanate ester. Polymer Engineering & Science, 2008. 48(7): p. 1322-1328.
6. de Abreu Corrêa, F., et al., Epoxidation of oleic acid catalyzed by PSCI-Amano lipase optimized by experimental design. Journal of Molecular Catalysis B: Enzymatic, 2012. 81: p. 7-11.
7. Kim, N., Epoxidation and di-hydroxylation of camelina sativa oil. 2014, Kansas State University.
8. Sinadinović-Fišer, S., M. Janković, and O. Borota, Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion exchange resin. Chemical Engineering and Processing: Process Intensification, 2012. 62: p. 106-113.
9. Milchert, E., A. Smagowicz, and G. Lewandowski, Optimization of the epoxidation of rapeseed oil with peracetic acid. Organic Process Research & Development, 2010. 14(5): p. 1094-1101.
10. Nikje, M.M.A., F. Abedinifar, and A. Idris, Epoxidized soybean oil ring opening reaction under MW irradiation. Applied Science Research, 2011. 3: p. 383-388.
11. Isa, M.T., et al., Epoxidation of methyl esters derived from Jatropha oil: An optimization study. Grasas y Aceites, 2012.
12. Dinda, S., et al., Epoxidation of cottonseed oil by catalysed by liquid aqueous hydrogen peroxide inorganic acids. Bioresource Technology, 2008. 99(9): p. 3737-3744.
13. Can, E., R. Wool, and S. Küsefoğlu, Soybean and castor oil based monomers: Synthesis and copolymerization with styrene. Journal of Applied Polymer Science, 2006. 102(3): p. 2433-2447.

_____

14. Kim, H.-M., et al., Biodegradable photo-crosslinked thin polymer networks based on vegetable oil hydroxy fatty acids. Journal of the American Oil Chemists' Society, 2010. 87(12): p. 1451-1459.

15. Ouyang, J., "Secondary doping" methods to significantly enhance the conductivity of PEDOT: PSS for its application as transparent electrode of optoelectronic devices. Displays, 2013. 34(5): p. 423-436.

16. Biswas, A., et al., Soybean oil as a renewable feedstock for nitrogen-containing derivatives. Energy & Environmental Science, 2008. 1(6): p. 639-644.

17. Liu, C., et al., Synthesis and properties of tung oil-based unsaturated co-ester resins bearing steric hindrance. Polymers, 2019. 11(5): p. 826.

18. Liu, W., et al., Soybean oil-based thermosets with N-vinyl-2-pyrrolidone as crosslinking agent for hemp fiber composites. Composites Part A: Applied Science and Manufacturing, 2016. 82: p. 1-7.

19. Eren, T., S.H. Küsefoğlu, and R. Wool, Polymerization of maleic anhydride–modified plant oils with polyols. Journal of applied polymer science, 2003. 90(1): p. 197-202.

20. Zhu, J., et al., Manufacturing and mechanical properties of soy-based composites using pultrusion. Composites Part A: Applied Science and Manufacturing, 2004. 35(1): p. 95-101.

21. Nugrahani, R.A., et al., Synthesis Of Compound–Containing Sulphonic Acid From Epoxidized Methyl Oleic of Rice Bran Oil and Linear Alkylbenzene Sulphonic Acid. Journal of Chemical Technology and Metallurgy, 2017. 52(5): p. 797-802.

22. Lubguban, A.A., et al., Functionalization via glycerol transesterification of polymerized soybean oil. Journal of applied polymer science, 2009. 112(1): p. 19-27.

23. Saba, N., et al., Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications. Journal of Reinforced Plastics and Composites, 2016. 35(6): p. 447-470.

24. Leveneur, S., et al., Interaction of thermal and kinetic parameters for a liquid–liquid reaction system: Application to vegetable oils epoxidation by peroxycarboxylic acid. Journal of the Taiwan institute of chemical engineers, 2014. 45(4): p. 1449-1458.

25. Patonay, T., É. Juhász-Tóth, and A. Bényei, Base-Induced Coupling of α-Azido Ketones with Aldehydes− An Easy and Efficient Route to Trifunctionalized Synthons 2-Azido-3-hydroxy Ketones, 2-Acylaziridines, and 2-Acylspiroaziridines. European Journal of Organic Chemistry, 2002. 2002(2): p. 285-295.

26. Stropoli, S.J. and M.J. Elrod, Assessing the potential for the reactions of epoxides with amines on secondary organic aerosol particles. The Journal of Physical Chemistry A, 2015. 119(40): p. 10181-10189.

27. Philippe, C., et al., Non Lewis acid catalysed epoxide ring opening with amino acid esters. Organic & biomolecular chemistry, 2009. 7(10): p. 2026-2028.

28. Kline and I. Company, Competitive intelligence for the global lubricants industry, 2004–2014. 2006, Kline & Company, Inc. Little Falls, New Jersey, USA.

29. Pop, L., et al., Basestock oils for lubricants from mixtures of corn oil and synthetic diesters. Journal of the American Oil Chemists' Society, 2008. 85(1): p. 71-76.

30. Pathak, V., D. Gupta, and N. Kumar, Studying Synthesis of Thermally and Chemically Modified Plant Oil and their tribological evaluation for use as a base stock for environmentally friendly bio-lubricant. 2014, SAE Technical Paper.

31. Pekol, S., Ecotoxicological assessment of metalworking fluids using the Allium cepa test procedure. Chemistry and Ecology, 2014. 30(1): p. 66-75.

32. Encinar, J.M., et al., Biolubricants from rapeseed and castor oil transesterification by using titanium isopropoxide as a catalyst: Production and characterization. Catalysts, 2020. 10(4): p. 366.

33. Dworakowska, S., D. Bogdal, and A. Prociak. Synthesis of polyols from rapeseed oil. in Proceedings of the 14th International Electronic Conference on Synthetic Organic Chemistry. 2010.

34. Dannecker, P.-K., Application of Catalytic Ester Reductions in Polymer Chemistry.

35. El-Din, M.N., et al., Studying the lubricity of new eco-friendly cutting oil formulation in metal working fluid. Industrial Lubrication and Tribology, 2018.

36. Benedicto, E., et al., Formulation of Sustainable Water-Based Cutting Fluids with Polyol Esters for Machining Titanium Alloys. Metals, 2021. 11(5): p. 773.

37. Santos, E.d.S., et al., The Lubricity Analysis of Cutting Fluid Emulsions. Materials Research, 2017. 20: p. 644-650.

38. Negm, N.A., et al., Eco-friendly vegetable oil-based metalworking fluid (MWFs) from modification of glycolyzed products of polyurethane. Journal of Surfactants and Detergents, 2016. 19(3): p. 455-466.

39. Pacheco, J.A., New nanoparticle water-based drilling fluid formulation with enhanced thermal stability and inhibition capabilities in the

_____

Woodford shale. 2018: Missouri University of Science and Technology.

40. Negm, N.A., et al., Novel nonionic polyurethane surfactants and Ag nanohybrids: influence of nonionic polymeric chains. Journal of Surfactants and Detergents, 2017. 20(1): p. 173-182.

41. Singh, Y., R. Garg, and S. Kumar, Comparative tribological investigation on EN31 with pongamia and jatropha as lubricant additives. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2016. 38(18): p. 2756-2762.

42. Karmakar, G., P. Ghosh, and B.K. Sharma, Chemically modifying vegetable oils to prepare green lubricants. Lubricants, 2017. 5(4): p. 44.

43. VALAKI, J.B., VEGETABLE OIL BASED METAL CUTTING FLUIDS FOR SUSTAINABLE MACHINING PROCESSES PROF. JANAK B. VALAKI, 2 MARADANIYA VISHAL, 3 VALA GAUTAM, 4 PATEL VIJAY, 5 RATHOD PRUTHVIRAJSINH.

44. Qin, G., et al., Synergistic Effect of Polyaspartate and Polyethylene Glycol on Lubrication Performance of the Water-Based Drilling Mud. ACS omega, 2021.

45. Aljeaban, N., et al., Polymers Decorated with Functional Motifs for Mitigation of Steel Corrosion: An Overview. International Journal of Polymer Science, 2020. 2020.

46. Center, I.W.R., Cutting Fluid Mangement: Small Machining Operations. 2003.

47. Negm, N.A., et al., Performance evaluation of cutting fluids additives developed from recycling of polyethylene terephthalate. J Appl Chem, 2014. 2: p. 69-79.

48. Tomoda, H., et al., Characteristic properties of cutting fluid additives derived from the reaction products of hydroxyl fatty acids with some acid anhydrides. Journal of Surfactants and Detergents, 1998. 1(4): p. 533-537.

49. Ali, Y. and M.A. Quraishi, Green Approaches to Corrosion Mitigation.

50. Selvam, M.D., V. Srinivasan, and C. Sekar, An attempt to minimize lubricants in various metal cutting processes. International Journal of Applied Engineering Research, 2014. 9(22): p. 7688-7692.