

Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives

Sujan Paul, Dibakar Roy, Pranab Ghosh*

Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

***Corresponding Author:** Pranab Ghosh, Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

Abstract: Growing environmental issues over the use of mineral oil based lubricants in automobile sectors have led to an increased attention towards the use of greener environmentally benign bio-lubricants. Working in this direction, the present report describes the synthesis of homopolymer of rapeseed oil and its copolymer with styrene. Characterization of the polymer was carried out by spectral (FT-IR, NMR), GPC and thermo gravimetric analysis. Biocompatibility and multifunctional performances [viscosity index improver, pour point depressant and antiwear] in lube oil compared to conventional additives was investigated using standard ASTM methods. Biodegradability was determined by disc diffusion and soil burial degradation method.

Keywords: Rapeseed oil, styrene, viscosity index improver, pour point depressant, antiwear, biodegradability.

1. INTRODUCTION

The base oil or the lubricating oils is usually of petroleum origin. It is a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons and the main function of it is to lubricate the engine components. The addition of additives to lubricating oil is very essential for smooth functioning of modern engines. Lubricants i.e. the suitable formulated product of lube oil and additives are generally liquids or semi-liquids and are used for the longevity and better performances of automotive engines. The key functions of a lubricant are to keep moving parts apart, reduce friction, protect against wear, transfer heat, prevent rust and corrosion, as antioxidant, as detergents/dispersants etc.

Although, the petroleum based lubricants exhibit satisfactory performance but they are not environmental benign due to their eco-toxicity and non-biodegradability. Strict regulations are, therefore, currently being imposed in a number of countries on lube oil-based lubricants together with their non-biodegradable toxic wastes materials (Betton et al., 2010). This increasing environmental awareness has provided researchers with the impetus to search for some new, environmentally benign, multifunctional additives. In this hunt, easily available vegetable oils have been considered as a potential candidate.

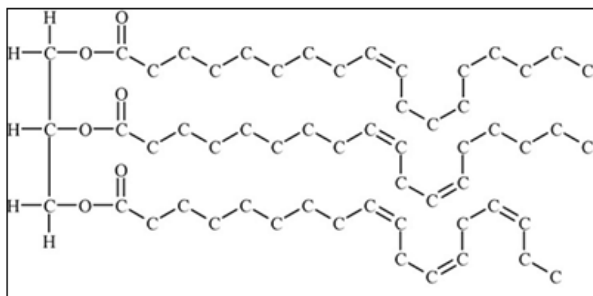
Moreover, they show excellent antiwear properties (Shanta et al., 2011), enhanced extreme pressure (EP) additive performance, exhibited high viscosity index (Ghosh et al., 2018) and low volatility (Sharma et al., 2009). There are lots of research papers where chemically modified vegetable oils have been used as additive for base oil or base stocks in the formulation of bio-lubricant (Karmakar et al., 2015).

Rapeseed oil (RO) is interesting for its richness in mono-unsaturated fatty acids, and for its low content in saturated fatty acids in comparison to other edible oils. Rapeseed oil is also frequently used in blends of vegetable oils (sunflower, soybean, corn, etc.) to improve the fatty acid profile of the vegetable oils. It has tremendous application in the field of nutritional and health claims. Apart from its above utilities, its unique composition and proven thermal stability over the other edible vegetable oils, points towards the additive properties of its suitably prepared polymers.

However research articles regarding such an application of RO as green multifunctional additive for lubricant are not yet reported.

Therefore, in this work we have synthesized homopolymer of RO (HRO) and copolymer of it with styrene in different percentage ratios to get thermally stable, cost effective as well as eco-friendly

multifunctional lubricant additives. Performance evaluation of the prepared polymeric additives was carried out as viscosity index improver, pour point depressant and antiwear according to respective ASTM method.



Molecular structure of rapeseed oil

2. EXPERIMENTAL SECTION

2.1. Materials

Rapeseed oil (about 90% unsaturation) was collected from a local grocer's shop. Toluene (GC 99.5%) was obtained from Merck Specialties Pvt. Ltd., (India). Benzoyl peroxide (LOBA chemie, India) was used after recrystallisation from chloroform- methanol mixture. Styrene (GC 99.8%, Thomas Baker Chemicals Pvt. Ltd., India) and the mineral base oil SN150 was collected from IOCL, Dhakuria, West Bengal, India. The physical properties of the rapeseed oil and base oil are shown in table 1. Fungal specimens were collected from the sister Department, Department of Microbiology, North Bengal University, West Bengal, India for testing the biodegradability of the polymers.

Table1. Properties of Rapeseed oil and Base oil

Rapeseed oil		Base oil	
Properties	Values	Properties	Values
Saponification index(mg/g)	167-74	Density at 313 K, kg.m ⁻³	868.03
Iodine index(mg/g)	97-100	Viscosity at 313 K	20.31×10
Refractive index at 50°C	1.462	Viscosity at 373 K	3.25 ×10
Density(g/ml)	0.916	Viscosity index	85
Saturated fatty acid (%)	7.36	Pour point (°C)	-6
Mono unsaturated fatty acid (%)	63.27	Cloud point (°C)	-8
Polyunsaturated fatty acid(%)	28.14	-	-
Oleic acid(g)	61.744	-	-
Linoleic acid ω-6(g)	19.005	-	-
α-Linoleic acid ω-3(g)	9.137	-	-

2.2. Synthesis of the Polymers

The copolymers were prepared by taking the monomers, RO and styrene at different ratios (table 2) in presence of BZP initiator by free radical polymerization method using toluene as solvent. The polymerization was accomplished in a three necked round bottom flask fitted with a magnetic stirrer, thermometer, condenser and an inlet for the introduction of nitrogen. In the flask, definite amount of rapeseed oil and styrene was heated to 80 °C and maintained for 20 minutes. Initiator BZP (0.5% w/w, with respect to the total monomer) was then added and refluxed for 6 hour. The detail procedure is mentioned in our previous publication (Ghosh et al., 2018).

Table2. Percentage composition and TGA values of the prepared polymers

Polymer Code	% Composition of monomers(w/w) in the feed		TGA values	
	RO	Sty	Decom. Temp.	PWL
P-1	100	0	160/320	28/78
P-2	98	2	210/355	24/85
P-3	96	4	266/382	17/80
P-4	94	6	268/382	19/81
P-5	92	8	268/384	18/79

RO = Rapeseed oil; Sty = Styrene; Decom. Temp.=Decomposition temperature; PWL= Percentage Weight loss.

2.3. Spectroscopic Measurements

NMR spectra were recorded on Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 and tetramethylsilane (TMS) was used as solvent and as reference material respectively. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} .

2.4. Molecular Weight Determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF at room temperature at a flow rate of 1mL/min.

2.5. Thermo Gravimetric Analysis (TGA)

TGA data was measured on Shimadzu TGA-50 system, at a heating rate of 10° C / min.

3. PERFORMANCE EVALUATION

3.1. Evaluation of Viscosity Index

The change of viscosity of the lubricant with increasing temperature is expressed in terms of a parameter called Viscosity index (VI). It was calculated according to ASTM D 2270-10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40 °C and 100 °C. The effect of additive concentration on VI was investigated by using different concentrations ranging from 1% - 5% (w/w).

3.2. Evaluation of Pour Point

Pour point of the additive blended lube oil was determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India).

3.3. Evaluation of Anti Wear Performance

The antiwear performance of the lubricant compositions in terms of wear scar diameter (WSD) was determined by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method. In this experiment 392 N (40 Kg) load at 75 °C for 60 min was applied to measure the wear scar diameter. The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively.

3.4. Biodegradability Test [dks]

Several tests have been devised for measuring the biodegradability of vegetable oil based additives, as they have an inherent biodegradability compared to the synthetic additives. In the present investigation it was tested by (a) the disc diffusion method against fungal pathogens (Ghosh et al., 2010) and (b) the soil burial degradation test.

3.5. Disc Diffusion (DD) Method

In this method, biodegradation of the prepared additives were tested against four different fungal pathogens, viz. *Colletotrichum camelliae* (CC), *Fusarium equiseti* (FE), *Alternaria alternata* (AA) and *Colletotrichum gloeosporioides* (CG) in a bacteriological incubator (Sigma Scientific Instruments Pvt. Ltd., India). Culture media for the fungal strains were prepared by mixing potato extract, dextrose, and agar powder in a 10:1:1 proportion by weight. 1.0 g of each of the polymeric additives were placed in Petri dishes with 2 g of the culture media and incubated at 310 K for 30 days with the different fungal pathogens. The fungal growth was confirmed by a change of colour from yellow to blackish. After 30 days, the additive samples were recovered from the fungal media and washed with chloroform, purified and dried. Finally, the weight loss for each of the samples was calculated.

3.6. Soil Burial Degradation Test (SBD Test)

In this test method the microorganisms attacks the surface of the polymer film (Liu et al., 2010). 1.0 g of each of the polymeric additive was taken to produce the polymer films. The films so obtained were then buried in soil (containing the microorganisms) in a bacteriological incubator. The soil was placed in a tray, the relative humidity was maintained to 50–60% with the help of a humidity chamber and the temperature was set at 303 K. The soil used in this study was taken from the campus of the North Bengal University (West Bengal, India) with pH 7.3 and moisture content of 25%. The buried polymer films

In the ^{13}C NMR of the copolymer, the peaks in the range of 14.14 - 41.03 ppm were due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the methine carbons of $-\text{CH}-$ of $-\text{COCH}-$ group. The peaks in the range of 60 - 62.08 ppm represent the carbons of $-\text{OCH}_2$ groups. The $-\text{CH}_2$ carbons of $-\text{OCOCH}_2-$ group of rapeseed oil showed peaks in the range of 64.61– 68.99 ppm. The aromatic carbons appear in the range of 127.93 -130.88 ppm. The peaks in the range of 165.65 - 173.00ppm confirms the carbons of ester carbonyl groups (**figure 3**).

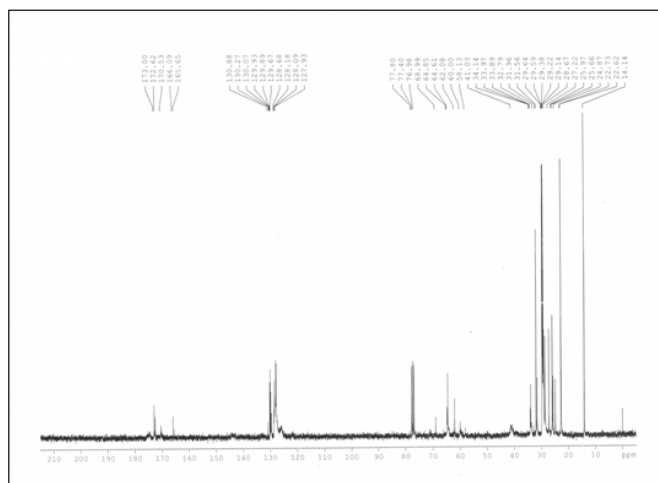


Figure3. A representative ^{13}C NMR spectra of rapeseed oil-styrene copolymer

In case of homopolymer of rapeseed oil, the IR absorption band at 1741 cm^{-1} (**figure 4**) showed the presence of ester carbonyl group. In the ^1H NMR spectra of homopolymer of rapeseed oil (**figure 5**), the peaks in the range of 4.12- 4.33 ppm indicate the protons of $-\text{COOCH}_2$ group of rapeseed oil, the methyl protons appear in the range of 0.86 - 0.90 ppm, the methylene protons in the range of 1.26 - 1.62 ppm and the methine protons appeared in the range of 2.29 - 2.34 ppm for the alkyl chains (**figure 5**). In the ^{13}C NMR spectra of homopolymer of rapeseed oil, the ester carbonyl group appears at 173.98 ppm, the carbons of $-\text{OOCH}_2$ group of appears at 62.07 – 68.91 ppm (**figure 6**).

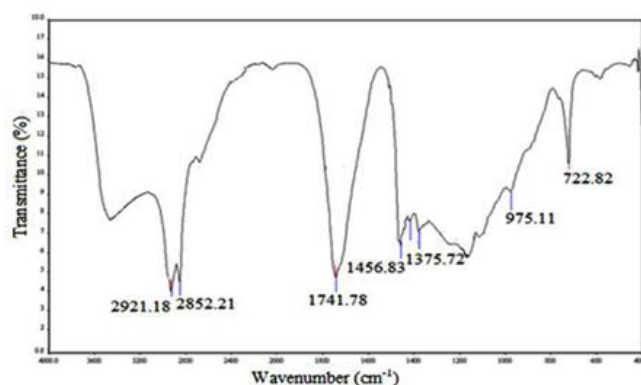


Figure4. FT-IR spectra of the homopolymer of rapeseed oil

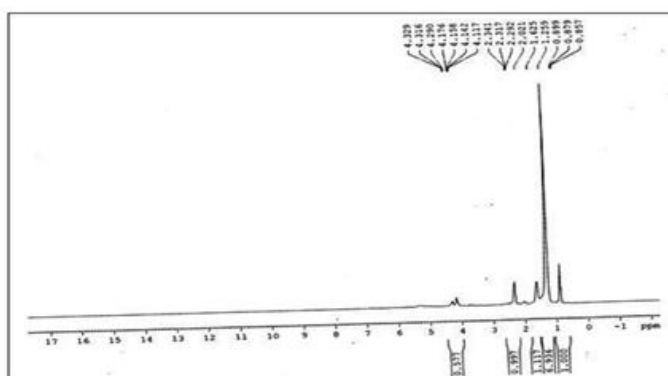


Figure5. ^1H - NMR spectra of homopolymer of rapeseed oil

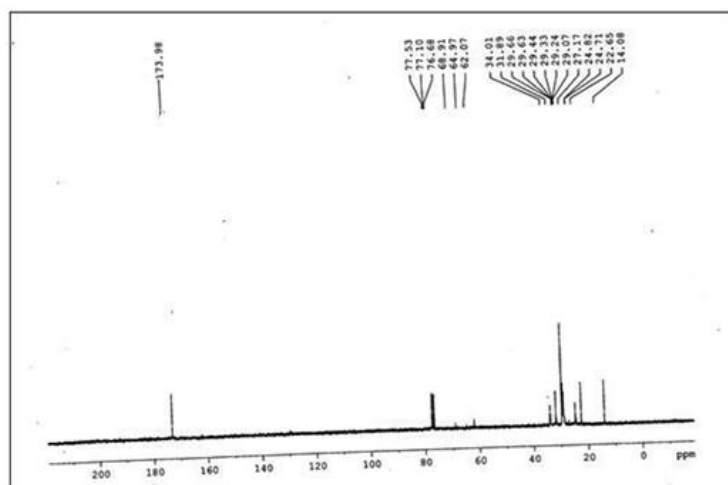


Figure6. ^{13}C - NMR spectra of homopolymer of rapeseed oil

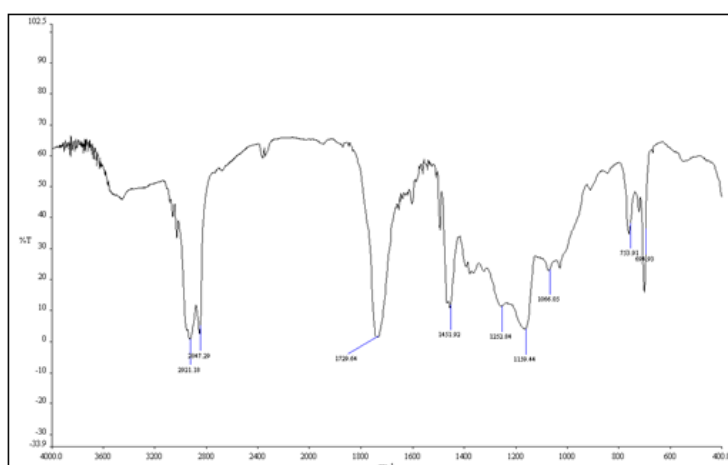


Figure7. A representative FT-IR spectrum of the copolymer after biodegradability test

4.2. Molecular Weight Data Analysis

The experimental values of number average molecular weights (M_n) and weight average molecular weights (M_w) of the prepared polymers (P-1 to P-5) are given in table 3. From the experimental data, it is seen that among the five polymers, P-5 has highest molecular weight. Moreover, it is also observed that with increasing the percentage of styrene in the backbone of rapeseed oil, the molecular weight increases. Therefore, percentage of styrene has a significant role during polymerization.

Table3. Molecular weight of the prepared polymers

Polymer Code	Average molecular weight (before biodegradation)			Average molecular weight (after biodegradation)		
	M_n	M_w	PDI	M_n	M_w	PDI
P-1	8328	11522	1.31	4132	4645	1.26
P-2	18657	26536	1.34	14211	21427	1.44
P-3	19497	29166	1.43	15512	24876	1.59
P-4	22671	33612	1.88	16536	29271	1.73
P-5	29654	38644	1.29	22320	29664	1.34

4.3. Analysis of TGA Data

The TGA values of the five polymers are given in table 2. From the table, it is clear that the thermal degradation of polymer P-1 is higher than the other polymers which signify that P-1 is thermally less stable. The thermal degradation of polymers P-3, P-4 and P-5 are almost similar. In case of polymer P-1, major decomposition starts at 160 °C with about 30% weight loss. For polymers P-3, P-4 and P-5, major decomposition starts approximately at 268 °C with 18% weight loss. Due to copolymerization of rapeseed oil with styrene, the thermal stability increases. Therefore, copolymerization with styrene has a significant importance to improve the thermal stability.

4.4. Analysis of Viscosity Index Values

VI was calculated at different concentrations ranging from 1% to 5% (w/w) to the base oil. The experimental values of VI are given in table 4. From the table, it is found that VI values increase with increasing the concentration of polymers in base oil. The viscosity of lubricating oil decreases with increasing temperature but expansion of polymer molecules take place with increasing temperature and due to this, the size of micelle increases. This increased in micelle size interfere the reduction of the viscosity of the lubricant (Tanveer et al., 2006). Moreover, with increasing the concentration of polymer in lubricating oil leads to an increase in the total volume of polymer micelle in lube oil and improves the VI property (Karmakar et al., 2013). It has been observed that VI value increases by incorporation of styrene in the backbone of homopolymer of rapeseed oil. This may be due to higher crosslink density of the copolymers. The copolymer P-5 has highest effect on VI increment followed by P-4, P-3, P-2 and P-1. The higher values VI in case of P-5 containing maximum percentage of styrene in the feed, are due to greater volume of the solvated additive molecule i.e. micelle compared to others which may be associated with its higher average molecular weights and lower PDI value.

Table4. Viscosity index (VI) values of polymer blended base oil

Polymer Code	VI of polymer blended base oil at different concentrations(w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85	89	95.5	104	112	118
P-2	85	94	98	112	115	128
P-3	85	96	104	114	123	131
P-4	85	101	106	116	124	133
P-5	85	103.5	111	125	135	145

4.5. Analysis of Pour Point Values

The pour points of the lubricants prepared by blending the polymers at different concentration levels ranging from 1%–5% (w/w) are shown in table 5. All the polymers are effective as PPD and the efficiency as pour point increases with increasing the concentration of polymers up to certain limit (4% concentration). This indicates that at this concentration, the polymer interacts with the paraffinic wax of base oil effectively and decreases the size of crystals of the paraffinic wax (El-Gamal et al., 1997). Among the prepared five polymers, P-4 showed better performance as PPD.

Table5. Pour point values of polymer blended base oil

Polymer Code	Pour point (° C) of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	-6	-9	-12	-12	-15	-16
P-2	-6	-10	-12	-16	-18	-16
P-3	-6	-10	-12	-16	-20	-18
P-4	-6	-12	-15	-18	-22	-24
P-5	-6	-10	-15	-18	-18	-22

4.6. Analysis of Anti Wear Properties

The tribological properties of the lubricant compositions were determined by measuring WSD through FBWT apparatus applying 392 N load and values are given in table 6. The anti wear performance of the lube oil is significantly improved when the polymers are blended with it and is reflected in the lower WSD values of the lubricant compositions. The copolymers showed better result compared to the homopolymer. The polymer P-5 at 5% concentration showed highest reduction in WSD values compared to the other polymers. This indicates that the film formed by the lubricant between the two moving metal surfaces is very strong. It may be due to higher molecular weight and hence higher number of polar side chains of the ester carbonyl groups and hydroxyl groups present in rapeseed oil (Masjuki et al., 1997). The contribution of higher percentage of styrene in the polymer feed has also played a significant role in it with its aromatic ring structure.

Table6. Antiwear property in terms of wear scar diameter (WSD in mm) values of different lubricant composition

Polymer Code	WSD of lubricant (in mm) at different polymer concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	1.116	1.067	1.044	1.025	1.007	0.964
P-2	1.116	1.065	1.037	1.023	1.003	0.957

P-3	1.116	1.060	1.028	1.018	0.992	0.955
P-4	1.116	1.052	1.022	1.002	0.958	0.931
P-5	1.116	1.031	1.013	0.992	0.943	0.911

4.7. Analysis of Biodegradability Test

Biodegradability test results (table 7) with the homo (P-1) and copolymers (P-2 to P-5) showed significant biodegradability against the fungal pathogens, *Calletotricheme camellia* and *Alternaria alternata*, though the result is, as expected, better for the homopolymer of rapseed oil. A close observation of the test results showed considerable biodegradation for all the samples. The analysis of the SBD tests indicated that the degradation of the additives studied increased continuously with the increasing number of days. Further, both the homo and copolymer of showed significant weight losses against the fungal pathogens, especially against *Alternaria alternate* (AA), in the DD test. Moreover, as expected for zero styrene content and owing to the presence of the natural monomer unit, the HRO (P-1) showed the highest biodegradability among all the additives in both of the tests. The FT- IR peaks of the polymer P-1 showed shift in the peak positions and considerable decrease in peak height and intensity after the DD test. The shift and the decrease in the IR peak intensities of the polymers before and after the biodegradation tests together with the PWL of the polymers confirmed the biodegradable nature of the prepared polymers.

Table7. Result of biodegradability test by the disc diffusion method and soil burial degradation.

Sample	Weight loss in disc diffusion method(g) [Pathogens used]					Weight loss in soil burial degradation (g)
	[CC]	[FE]	[AA]	[CG]	[CE]	
P-1	0.45	0	0.62	0	0	0.47
P-2	0.38	0	0.54	0	0	0.35
P-3	0.30	0	0.48	0	0	0.30
P-4	0.26	0	0.39	0	0	0.25
P-5	0.22	0	0.35	0	0	0.19

CC = Calletotricheme camellia; FE = Fussarium equisitae; AA = Alternaria alternata; CG = Colletrichum gleosporoides; CE= Curvularia eragrostidies.

5. CONCLUSION

From the above study it was found that the copolymer of rapeseed oil with styrene showed excellent multifunctional performance for base oil. As a viscosity index improver, pour point depressant and antiwear additive, the copolymers are found more effective than the homopolymer. In addition, the presence of rapseed oil in the additive composition introduces excellent biodegradability too, in the additive. Average molecular weight and thermal stability of the copolymers increases with the increase in the percentage of styrene. Therefore, the above study is definitely a potential approach to formulate a greener lubricant composition with excellent multifunctional additive properties for lube oil.

ACKNOWLEDGEMENT

The authors thank to UGC, New Delhi for financial support. Special thanks to IOCL, India for providing the base oil.

REFERENCES

- [1] Betton CI (2010) Lubricants and Their Environmental Impact. In: Chemistry and Technology of Lubricants, Eds. Mortier RM, Fox MF, Orszulik ST, Springer, The Netherlands, pp. 435-457.
- [2] Chandure AS, Umare SS (2007) Synthesis, Characterization and Biodegradation Study of Low Molecular Weight Polyesters. *Int J Polym Mater* 56: 339–353.
- [3] El-Gamal, I.M., Atta, A. M., and Al-Sabbagh, A. M. (1997). Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* 76:1471–1478.
- [4] Ghosh, P., Hoque, M., and Karmakar. G. (2018). Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. *Polym. Bull.* 75:501-514
- [5] Ghosh P, Das T, Nandi D, Karmakar G, Mandal A (2010) Synthesis and characterization of biodegradable polymer: Used as a pour point depressant for lubricating oil. *Int J Polym Mater* 59: 1008–1017
- [6] Karmakar, G., and Ghosh, P. (2013). Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* 1:1364–1370.

- [7] Karmakar, G., and Ghosh, P. (2015). Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* 3: 19–25.
- [8] Ghosh P, Karmakar G (2014) Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int J Ind Chem* 5: 7
- [9] Liu M, Huang Z, Yang Y (2010) Analysis of biodegradability of three biodegradable mulching films. *J Polym Environ* 18: 148–154.
- [10] Masjuki, H. H., Maleque, M. A. (1997). Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* 206: 179 –186.
- [11] Shanta, S. M., Molina, G. J., and Soloiu, V. (2011). Tribological effects of mineral-oil lubricant contamination with biofuels: A pin-on-disk tribometry and wear study. *Adv. Tribol.* doi:10.1155/2011/820795.
- [12] Sharma, B. K., Adhvaryu, A., and Erhan, S. Z. (2009). Friction and wear behavior of thioether hydroxyl vegetable oil. *Wear* 42:353–358.
- [13] Tanveer, S., Sharma, U. C., and Prasad, R. (2006). Rheology of multigrade engine oils. *Indian J. Chem. Technol.* 13:180–184.

Citation: *Sujan Paul, Dibakar Roy, Pranab Ghosh, “Greener Lubricant Formulation: Rapeseed Oil Based Eco-Friendly Lube Oil Additives”, International Journal of Petroleum and Petrochemical Engineering, 6(3), pp. 29-37. DOI: [https:// doi.org/10.20431/2454-7980.0603004](https://doi.org/10.20431/2454-7980.0603004)*

Copyright: © 2020 Authors, this is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.