Journal of Scientific & Industrial Research
Vol. 79, June 2020, pp. 537-540

Castor Oil and Acrylate based Copolymer as Green Additive for Lubricating Oil

Mainul Hoque, Dibakar Roy and Pranab Ghosh*

Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling 734 013, India

Received 17 May 2019; revised 11 December 2019; accepted 7 April 2020

In this work, the authors synthesized three different acrylates by esterification reaction of acrylic acid with three different long chain alcohols (octan -1-ol, decan -1-ol and dodecan -1-ol). Homopolymer of castor oil (CO) and three copolymers of castor oil with acrylates were prepared by free radical polymerization method in the presence of azobisisobutyronitrile (AIBN) as initiator. FT-IR and NMR spectral technique were used to characterize the synthesized polymers. The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by gel permeation chromatography (GPC) method. Thermo gravimetric analysis (TGA) method was used to study the thermal behaviour of the prepared polymers at high temperature. Performances of the polymers as additives in lubricating oil were carefully assessed in terms of viscosity index and pour point. The experimental results showed that the prepared copolymers are better additives than homopolymer. Disc diffusion method was applied to carry out the biodegradability test of all the prepared polymers.

Key words: Esterification, Homopolymer, Viscosity index, Biodegradability

Introduction

The lube oil additives synthesized from acrylate, maleic anhydride, vinyl acetate etc exhibit better performance but they are not environmentally benign. It is due to their inability to biodegradation. The application of bio-based products for the synthesis of lube oil additives has solved this problem. The additives synthesized from vegetable oils have potential advantages compared to the synthetic additives owing to their less toxic and biodegradable properties.[1] They have high viscosity index (VI)[2], low pour point, excellent antiwear property[3] and low volatility.[4] So, the application of additives derived from vegetable oils for base oil to formulate green lubricant composition has found greater attraction recently.

Castor oil is obtained from castor seeds which is available in nature. It comprises 85–95% triacylglycerol of ricinoleic acid which is a C-18 fatty acid having a double bond at C-9 and a hydroxyl group at C-12. Due to trifunctional nature of castor oil, it can be used as a monomer for the preparation of lube oil polymeric additives as well as base stock also.[5,6]

The present work comprises preparation of homopolymer of castor oil and different copolymers with octyl acrylate, decyl acrylate and dodecyl acrylate to get better performing and thermally more stable green lubricant additives. Performance of the polymers was evaluated as viscosity index improver (VII) and pour point depressant (PPD) additives in mineral base oil according to respective standard ASTM method.

Materials and Methods

Experimental Section

Preparation of esters

Octyl acrylate (OA), decyl acrylate (DA) and dodecyl acrylate (DDA) were prepared by reacting acrylic acid with octan -1-ol, decan -1-ol and dodecan -1-ol respectively in the molar ratio of 1.1:1 in the presence of conc. H_2SO_4 as a catalyst, 0.25% (w/w) hydroquinone with respect to the total reactants as polymerization inhibitor and toluene as solvent by using Dean Stark apparatus. The details of esterification reaction and the purification were carried out by the procedure as reported in the earlier publication.[7]

Synthesis of the polymers

The copolymers were synthesized by free radical polymerization method taking the monomers of castor oil (95%, w/w) and acrylate (5%, w/w) in presence of AIBN as initiator. The polymerization reaction was

*Author for Correspondence
E-mail: pizy12@yahoo.com

completed in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the passing of nitrogen. The mixture of castor oil and acrylate was heated to 80°C without any solvent. Initiator AIBN (0.5% w/w, with respect to the total monomer) was then added and continuously heated for 5 hour keeping the temperature constant at 80°C. After the completion of reaction, the product was poured into methanol with continuous stirring, filtered off and dried. The homopolymer of castor oil was also prepared in the similar procedure. The prepared homopolymer and three copolymers with OA, DA and DDA are designated as P-1, P-2, P-3 and P-4 respectively.

Spectroscopic measurements

Bruker Avance 300 MHz FT-NMR spectrometer was used to record the NMR spectra and $CDCl_3$ was used as solvent. IR spectra were documented on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1}.

Molecular weight determination

The average molecular weight was recorded by GPC method (Water 2414) in HPLC grade THF at 35°C at a flow rate of 1 mL/min.

Thermo gravimetric analysis (TGA)

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

Performance Evaluation

Evaluation of viscosity index

Viscosity index (VI) is an important parameter to determine the change of viscosity of the lubricant composition with increasing temperature. Higher the value of VI, smaller is the change of viscosity at high temperature. It was calculated according to ASTM D 2270-10. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are required to calculate the VI.

Evaluation of Pour point

Pour point values of the lubricant composition were measured according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). A good pour point depressant additive lowers the pour point of the lubricant composition to a larger scale.

Biodegradability test (Disc diffusion method)

The biodegradability test was carried out for the prepared polymers against Alterneria alternata fungal. Culture media strain was made by mixing a suitable amount of potato extract, dextrose and agar powder. All the experiments were completed in petri dishes and were kept in incubator at 37°C for 30 days after addition of about 2 g of the polymer sample. The fungal growth was confirmed by a change of yellow to blackish colour. After 30 days, the fungal media was dissolved in chloroform and the polymer samples were recovered, purified and dried. The dried samples were weighed.

Results and Discussion

Spectroscopic analysis

The homopolymer of castor oil showed IR absorption band for the ester carbonyl group at 1735.1 cm^{-1}. The peaks at 2854.4 cm^{-1} and 2922.2 cm^{-1} are the stretching vibration of CH_3-CH_2- group. A broad peak at 3442.9 cm^{-1} is due to –OH group present in castor oil. The IR spectra of three copolymers (P-2 to P-4) are almost similar. The absorption band at 1732.08 cm^{-1} is due to ester carbonyl group.

In the ^1H NMR spectra of homopolymer, the peaks in the range of 4.12–4.323 ppm indicate the protons of –$COOCH_2$ group of castor oil and the peaks in the range of 3.60–3.72 ppm indicate protons of –OH group of castor oil. In case of copolymer, the peaks in the range of 1.616–2.318 ppm indicate the protons of - COCH- group of alkyl acrylate. Peaks at 3.607–3.656 ppm indicate the protons of – OCH_2 of acrylate moiety. The peaks in the range of 3.988–4.156 ppm indicate the protons of – $COOCH_2$ group of castor oil. No peaks in the range of 5–6 ppm indicate that both homo and copolymerization was carried out successfully.

In the ^{13}C NMR spectra of homopolymer, the peaks in the range of 172.95–177.41ppm indicate the carbons of ester carbonyl group. The carbons of –$OOCH_2$ group appear in the range 62.10–68.86 ppm. In case of copolymer, the peak at 58.11 ppm indicates the carbons of –OCH_2 groups of acrylate moiety. The carbons of –$OOCH_2$ group of castor oil appear at 62.78–64.87 ppm. The peaks ranging from 166.31–174.63 ppm confirm the presence of carbons of ester carbonyl groups. There is no any peak in the range of 120–150 ppm and it indicates that both homo and copolymerization was completed successfully.

Molecular weight data analysis

The experimental data of number average molecular weight (M_n), weight average molecular weight (M_w) of the polymers (P-1 to P-4) are shown in Table 1**.** From the data, it is been observed that among the four polymers, P-1 and P-4 have the lowest and highest molecular weight respectively. Moreover, it is also observed that with increasing the alkyl chain length of the acrylate moiety in the copolymers, the molecular weight increases. Therefore, length of alkyl group in acrylate moiety has an important role during copolymerization.

Analysis of TGA data

From the experimental TGA values of the four polymers, it was observed that polymer P-1 is thermally less stable than the prepared copolymers. This indicates that when acrylate moiety is introduced in the backbone of castor oil, the thermal stability increases. Two major decompositions have been observed at 150°C and 300°C with 25% and 80% weight loss respectively in case of P-1. The thermal stability of copolymers P-2, P-3 and P-4 are almost identical where two major decompositions were observed at 185°C and 358°C with 18% and 78% weight loss respectively.

Analysis of viscosity index values

VI of lubricant composition was calculated at different concentration levels ranging from 1% to 5% (w/w). The experimental values of VI are listed in Table 2. As the temperature increases, the viscosity of lube oil decreases but expansion of polymer molecules take place from tight coil due to increased lube oil - polymer interaction. As a result, the size of micelle increases and this increased in micelle size prevents the reduction of the viscosity of the lubricant composition. It is observed that a higher polymer concentration showed a higher viscosity index compared to a lower one since the total volume of polymer micelle in lubricant increases and hence improves the VI property.[1] It is observed that VI increases by incorporation of acrylate moiety in the backbone of homopolymer of castor oil. This may be due to higher molecular weight and higher crosslink density of the copolymers. The copolymer P-4 has highest VI value than the other polymers, P-3, P-2 and P-1. It may be due to higher average molecular weight compared to others.

Table 1 — 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	7928	10022	1.26	4814	5465	1.14
P-2	8948	17515	1.96	7624	13503	1.77
P-3	10972	18048	1.64	9256	14592	1.58
P-4	16246	24228	1.49	15337	20016	1.31

M_n = Number average molecular weight; M_w = Weight average molecular weight;
PDI = Polydispersity index

Table 2 — Viscosity index (VI) values of lubricants

Polymer Code	VI of lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	85.2	90	94.5	102	112	116
P-2	85.2	98	104	116	122	134
P-3	85.2	100	108	116	128	138
P-4	85.2	100	112	123	135	145

Analysis of Pour point values

The pour points of the lubricant composition at different concentration levels ranging from 1%−5% (w/w) are tabulated in Table 3 which indicates that the prepared lubricants have lower PP than lube oil and hence the prepared polymers can be used as PPD additive. From the experimental data, it is observed that the efficiency as PPD increases up to certain limit (3% concentration). The reason for this may be, at this concentration the additive interacts with the paraffinic wax of lube oil effectively and decreases the shape of crystals of the paraffinic wax.[8] Among the prepared four polymers, P-2 showed best performance as PPD. The higher PDI value may be the reason for better performance.[9]

Analysis of biodegradability test results

The fungal Alterneria alternata was used to carry out the biodegradability test. It was found that homopolymer (weight loss 58%) is more biodegradable than the copolymers (weight loss 42%).

Table 3 — Pour point values of lubricants

Polymer Code	Pour point (0°C) lubricant at different concentrations (w/w)					
	0%	1%	2%	3%	4%	5%
P-1	–6	–9	–12	–14	–15	–15
P-2	–6	–10	–15	–21	–21	–21
P-3	–6	–10	–13	–18	–18	–18
P-4	–6	–10	–13	–17	–17	–17

After biodegradation, the molecular weight of the recovered polymers was also determined by GPC method and the results were compared with the respective polymers before biodegradation and listed in Table 1.

Conclusions

From the above study, it is found that the homopolymer and copolymer of castor oil are effective additives as viscosity index improver and pour point depressant for lubricating oil. Copolymers are more effective than homopolymer. Thermal stability and average molecular weight of copolymers increase with increasing the alkyl chain length of acrylate moiety. Due to biodegradability character, the additives are environmentally benign also. Therefore, this study is definitely a potential approach to formulate a green additive for lubricating oil.

Acknowledgement

The authors thank to UGC, New Delhi for financial support and thank also to IOCL, India for providing the lubricating oil.

References

1 Karmakar G & Ghosh P, Green additives for lubricating oil, *ACS Sustainable Chem Eng*, **1** (2013) 1364−1370.

2 Balamurugan K, Knangasabapathy N & Mayilsamy K, Studies on Soyabean oil based lubricant for diesel engine, *J Sci Ind Res*, **69** (2010) 794–797.

3 Kumar G S, Balamurugan A, Vinu S, Radhakrishnan M & Senthilprabhu G, Tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester, *J Sci Ind Res*, **71** (2012) 562–565.

4 Samarth N B & Mahanwar P A, Modified vegetable oil based additives as a future polymeric material—Review, *Open J Org Polym Mater*, **5** (2015) 1–22.

5 Ghosh P, Hoque M & Karmakar G, Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant, *Polym Bull*, **75** (2018) 501–514.

6 Chinchkar D S, Satpute S T, & Kumbhar N R, Castor oil as green lubricant: A Review, *Int J Eng Res Technol*, **1** (2012) 1–3.

7 Ghosh P, Das M, Upadhyay M, Das T & Mandal A, Synthesis and Evaluation of Acrylate Polymers in Lubricating Oil, *J Chem Eng Data*, **56** (2011**)** 3752–3758.

8 Al-Sabagh A M, Sabaa M W, Saad G R, Khidr T T & Khalil T M, Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties, *Egypt J Petrol*, **21** (2012) 19–30.

9 Ghosh P, Hoque M & Nandi D, Homo and copolymers of decyl methacrylate as performance additives for lube oil, *Pet Sci Technol*, 33 (2015) 920–927.