



Castor Oil and Acrylate based Copolymers as Greener Additives for Lubricating Oil

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Received 15 February 2020; revised 22 April 2020; accepted 24 September 2020

In this work, the authors synthesized three different acrylates by esterification reaction of acrylic acid with long chain alcohols (octyl alcohol, decyl alcohol and dodecyl alcohol). Homopolymer of castor oil (CO) and three copolymers of castor oil with acrylates were synthesized by free radical polymerization using azobisisobutyronitrile (AIBN) as initiator. FT-IR and NMR spectral technique were used to characterize the synthesized polymers. The average molecular weight was determined by gel permeation chromatography (GPC). Thermo gravimetric analysis (TGA) method was used study the thermal behaviour of the 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 biodegradability test of all the prepared polymers.

Keywords: Biodegradability, Copolymer, Esterification, Homopolymer, Viscosity index

Introduction

The lube oil additives synthesized from acrylate, maleic anhydride, vinyl acetate etc although exhibit satisfactory performance but they are not environmental benign due to their eco-toxicity and non-biodegradability. The application of bio-based resources for the preparation of additives has solved this problem and simultaneously reduces environmental impacts significantly. Vegetable oils based additives have greater advantages compared with synthetic additives owing to their biodegradable properties and low-toxicity.¹ They have high viscosity index (VI)², low pour point, excellent antiwear property³ and low volatility.⁴ So, the application of additives derived from vegetable oils for base oil to develop environmental green lubricant framework has got importance recently.

Castor oil is obtained from castor seeds which is available in nature. It consists of 85-95% triacylglycerol of ricinoleic acid having C-18 fatty acid chain. It has a double bond at C-9 and a hydroxyl group at C-12. Due to presence of three active sites, it can be used as a monomer for the preparation of additives for lubricating oil and as a base stock also.^{5,6}

The present work comprises synthesis of homopolymer of castor oil and different copolymers

with octyl acrylate, decyl acrylate and dodecyl acrylate to get thermally stable, better performing green lubricant additives. Evaluation of efficiency of the polymers as viscosity index improver (VII) and pour point depressant (PPD) additives in mineral lube oil were carried out according to respective standard ASTM methods.

Experimental Details

Preparation of Esters

Octyl acrylate (OA), decyl acrylate (DA) and dodecyl acrylate (DDA) were prepared by reacting acrylic acid with octyl alcohol, decyl alcohol and dodecyl alcohol respectively in the molar ratio of 1.1:1 in the presence of conc. H₂SO₄ 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 procedure of esterification and its 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 initiator. The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. The mixture of castor

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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. CDCl₃ 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 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 essential to calculate the VI.

Evaluation of Pour Point

Pour point of the lubricant composition was determined 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 *Alternaria alternata* fungus. Culture media was prepared by mixing

suitable amount of potato extract, dextrose and agar powder. All the experiments were completed in petridishes and were kept in incubator at 37°C for 30 days after addition of about 2g of the polymer sample. The fungal growth was confirmed by a change of yellow to blackish colour. After 30 days, the polymer samples were recovered from the fungal media by chloroform, 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 CH₃-CH₂- 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 -COOCH₂ 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 -OCH₂ of acrylate moiety. The peaks in the range of 3.988–4.156 ppm indicate the protons of -COOCH₂ 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 ¹³C NMR spectra of homopolymer, the peaks in the range of 172.95–177.41 ppm indicate the carbons of ester carbonyl group. The carbons of -OOCH₂ group appear in the range 62.10–68.86 ppm. In case of copolymer, the peak at 58.11 ppm indicates the carbons of -OCH₂ groups of acrylate moiety. The carbons of -OOCH₂ 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 groups. There is no any peak in the range of 120–150 ppm and it indicates that both homo and copolymerization was carried out 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 experimental 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, alkyl chain length of acrylate has a significant 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 concentrations ranging from 1% to 5% (w/w). The experimental values of VI are listed in Table 2. The viscosity of lube oil decreases with increasing temperature 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. This increased in micelle size prevent 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.

Analysis of Pour Point (PP) 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

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

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

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. It may be due to higher PDI value.⁹

Biodegradability Test Results

The fungus *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%). 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 shown 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, the additives are environmentally benign also. Therefore, this study is definitely a potential approach to develop an environmentally benign lubricant composition.

Acknowledgement

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

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