



Copolymers of Castor and Corn Oils with Lauryl Methacrylate as Green Lubricating Additives

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Abstract

During the last few years, the greener additives prepared from bio-raw materials with low-cost and multifunctional applications have attracted considerable attention in the field of lubricant industry. In the present work, copolymers derived from castor and corn oils with decyl methacrylate were prepared by free radical polymerization using benzoyl peroxide (BPO) as a thermal initiator. Direct polymerization of fatty acid double bonds results in the development of environmentally friendly copolymeric additives (Co-1 and Co-2). The resulting copolymers were characterized by Proton Nuclear Magnetic Resonance (¹H-NMR) and Fourier Transform Infrared (FTIR). Thermogravimetric analysis was employed to determine the thermal decomposition of copolymers. The average molecular weight was measured by gel permeation chromatography (GPC) method. Different concentrations of prepared copolymer as additives *vis* 1, 2, 3, and 4 (w/v) were used to examine the performance evaluation and rheological behavior of the formulated base oil. The prepared copolymers show good thermal stability. Both prepared polymeric additives (Co-1 and Co-2) are evaluated as pour point depressant and excellent viscosity improver. The base oil blended with Co-1 has higher viscosity index value than the lubricant oil mixed with Co-2. The values of pour point for the lubricant oil blended with Co-1 and Co-2 are ranging from (-11 to -15 °C) and (-12 to -15 °C), respectively.

Keywords: Multifunctional green additives; Pour Point Depressant; Viscosity Index improver; Copolymers.

1. Introduction

Lubricants are the materials (generally liquids, but may be solids or semi-solids) used to lubricate machinery parts to reduce friction and increase their lifetimes [1, 2]. Lubricants are made up of a variety of base fluids and chemical additives and play an important role in tribology. Some significant additives include corrosion inhibitors, viscosity index improver, dispersant, detergent, antiwear, antioxidants, and pour point depressant. Since the diversity of fluidity and viscosity with temperature is a significant principle that defines the relevance of lubricant construction at thrilling temperature conditions, depressants of pour point [3, 4] and improvers of viscosity index [5, 6] additives are the most widely used.

In the last few years, many kinds of additives are utilized such as viscosity modifiers [7, 8] and pour

point depressants, but most of them are based upon synthetic acrylates. They are not getting much importance to be used in this field due to their toxicity. As a result, the manufacture of biodegradable and environmentally friendly additives is a primary anxiety in the lubricant industry [9, 10]. Additives synthesized from sustainable feedstocks, such as vegetable oil, are encouraging replacements because of their ecofriendly, excellent lubricity, low volatility and biodegradability, making them ideal for use in lubricants.

In the past, significant studies have been achieved to prepare new multifunctional spices using sustainable starting materials, e.g. the conduct of additives synthesized from dodecyl acrylate and sunflower oil have been studied by Ghosh et al., the synthesized additives behaved as a pour point depressant and viscosity modifier for the lubricant oil

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Receive Date: 05 February 2021, Revise Date: 28 March 2021, Accept Date: 07 April 2021

DOI: 10.21608/EJCHEM.2021.61665.3327

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[11], copolymeric additive designed from styrene and dodecylacrylate shown to be very effective pour point depressant and viscosity modifier. Polyol additives synthesized from epoxidized vegetable oil have been developed by Campanella et al. to show excellent viscosity temperature relationship [12]. Additives based on castor oil and dodecyl acrylate copolymer shows multifunctional performance for lubricant oil. In addition, the compounds derived from improved rapeseed oil also establish to be active as an ecofriendly material for rapeseed oil [13]. Finally, a strategy developed by Ghosh et al. shows that soybean-methyl acrylate additive act as better depressant of pour point whereas additive of soybean oil with styrene and decene perform as well modifier of viscosity [14]. As a result, in order to produce novel biodegradable and eco-friendly additives, corn and castor oils were chosen along with lauryl methacrylate. Copolymer-based materials utilized in the industry of lubricant motivated our research. As a result, the aim of this research is to improve polymeric green additives based on renewable raw material, such as castor and corn oils, as well as lauryl methacrylate. Standard methods were used to evaluate their physicochemical and rheological properties. The objective of this template is to enable you in an easy way to style your article attractively in a style similar to that of *EJCHEM*. It should be emphasized, however, that the final appearance of your paper in print and in electronic media will very likely vary to some extent from the presentation achieved in this Word® document.

2. Materials and Methods

2.1. Materials

Castor and corn oils were gotten from the local market; lauryl methacrylate was obtained from Merck and was used without additional purification. The initiator (BPO) from Merck was purified by twice recrystallizations from chloroform and refrigerated prior to use. Toluene (GC 99.5%) and ethanol (AR 99.9%) were purchased from Sigma Aldrich and used as received. The lubricating oil was collected from Total oil corporation ltd., Baghdad.

2.2. Technique

Synthesis of copolymers (Co-1 and Co-2)

To the solution of castor oil (9.3 g, 10 mmol) in toluene (10 mL), a lauryl methacrylate (7.6 g, 30 mmol) with 1:3 molar ratios was added. The reaction mixture was continuously stirred and preheated at 90 °C for 60 minutes. The initiator used as benzoyl peroxide (0.5% w/w, with respect to the total monomers) was then added and continuously heated for 12 hours keeping the temperature constant at 80°C. The reaction was then cooled before being stopped by dumping the reaction mixture into the ethanol. Decantation with ethanol was employed to remove the unreacted starting material. The furnished colourless viscous copolymer was then obtained in a 91% yield. Similarly, Co-2 was synthesized from corn oil and lauryl methacrylate by following the above-mentioned method. The Co-2 additive was attained in 95% yield. Alternatively, you may insert the whole text or parts you previously prepared by using on the 'Insert' menu of Word® the option 'File...'. In that case take care to retain the above mentioned section breaks. After the file is inserted you can style it by placing the cursor in each paragraph and clicking the required style on the drop-down menus.

2.3. Characterizations

Spectroscopic Analysis

FTIR Spectra of the copolymers was recorded at room temperature using a Perkin Elmer-1650 spectrometer and KBr Pellets in the wavenumber range of 200-4000 cm^{-1} . JOEL JMTC-500/54/SS (500 MHz) spectrometer was employed to record the $^1\text{H-NMR}$ spectra using (TMS) as an internal reference solution and (DMSO) as a solvent and tetramethyl silane.

Thermogravimetric Analysis (TGA)

Perkin Elmer in a nitrogen atmosphere at a heating rate of 10 °C/min from 0 to 800 °C was used to study the thermal degradability of the copolymers. With an increase in temperature, the percentage of weight loss (PWL) of the additives was conducted.

Molecular weight determination

The number average and weight average molecular weights (M_n and M_w) of the synthesized copolymers Co-1 and Co-2 were measured in Water's gel permeation chromatography. Furthermore, the distribution of molecular weight (polydispersity

indices) of the additives was determined using polystyrene standards and tetrahydrofuran (THF) as a mobile phase at a flow rate of 1.0 mL/min at 35 °C.

2.4. Formulation of Additives

The prepared copolymers, namely Co-1 and Co-2, were readily soluble in lubricating base oil. The copolymers were mixed in weight/volume ratios of 1%, 2%, 3%, and 4%. The copolymeric materials have been tested for performance evaluation after the formulation of the lubricant.

2.5. Evaluation of Viscosity Index

Ostwald viscometer was employed to determine the kinematic viscosity of the base oil and formulated lubricant according to the ASTM D445 standard method using toluene as standard solvent at 40 and 100 °C. Counting the time flow of at least five various concentrations of sample solutions was used to make the experimental determination. Chronometer was manually used to calculate the time flow of the solution [15]. The ASTM 2270-93 method was then used to calculate the viscosity index.

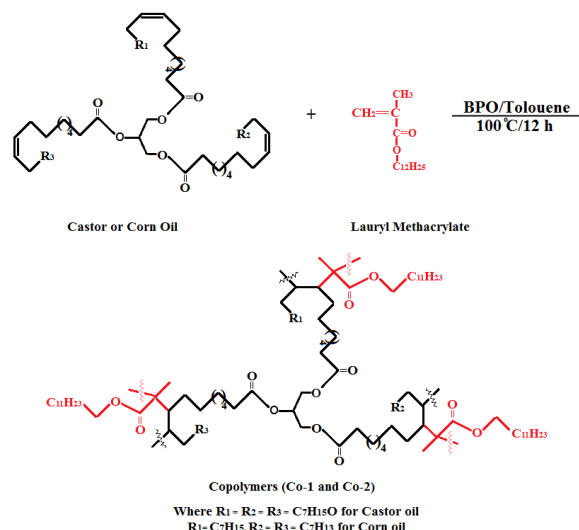
2.6. Evaluation of Pour point

The standard ASTM D-97 method was used to determine the cloud and pour points of lubricant oil without and with copolymeric additives (Co-1 and Co-2) at various concentrations. The experimental data was collected by averaging the findings of three separate experiments conducted under identical conditions. A good pour point depressant addition reduces the base oil composition's pour point on a broader scale.

3. Results and Discussion

The renewable raw materials such as castor oil and corn oil were chosen and favored because they contain a higher level of unsaturation, making them ideal for additive synthesis. Castor oil contains 1-5% linoleic acid, 2-6% oleic acid, and 85-95% ricinoleic acid in its fatty acid composition whereas corn oil contains 27.3% oleic acid and 58% linoleic acid. We envisaged that a free radical polymerization technique could be employed to synthesize the polymeric additives (Co-1 and Co-2). It was observed that benzoyl peroxide (BPO) decomposed under thermal conditions to generate benzene free radicals, which is responsible for the initiation step of the

copolymerization between lauryl methacrylate and triglyceride of castor oil. It was then accompanied by chain propagation, and finally the reaction was terminated by pouring the mixture into an ethanol solution to obtain the sunflower oil copolymer. Similarly, lauryl methacrylate was used to make a corn oil copolymer (Scheme 1).



Scheme 1. Schematic illustration of the process formation of (Co-1 and Co-2) copolymers from castor and corn oils with lauryl methacrylate.

3.1. Spectroscopic data analysis

The prepared copolymers were further characterized by routine spectroscopic analysis. The FTIR absorptions between 1740–1700 cm^{-1} indicates the presence of ester carbonyl group for copolymer Co-1 and Co-2, respectively (Figure 1). The peaks between 1152–1159 cm^{-1} resembles C–O stretching frequency of ester carbonyl in both the copolymers, 740–655 cm^{-1} indicates C–H bending vibrations, 2911–2842 cm^{-1} confirms the presence of paraffinic CH stretching frequency of CH_3 and CH_2 groups. In case of Co-1, the peak at 3500 cm^{-1} belongs to hydroxyl group of castor oil. Furthermore, absence of olefinic double bond peak in Co-1 and Co-2 while its presence in the respective monomers at about 1610 cm^{-1} supports the formation of polymers. The FT-IR spectra confirms the production of a copolymer and is in close accord with a previous investigation [16].

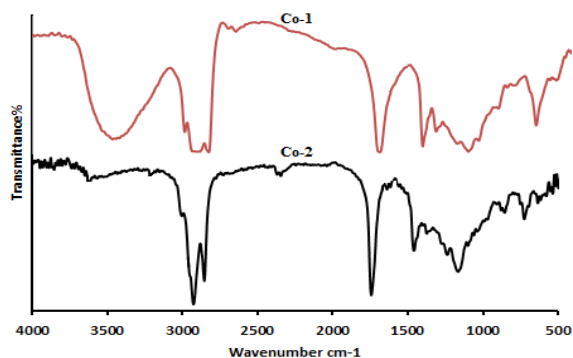


Fig. 1. FT-IR spectra of the copolymeric additives Co-1 and Co-2

$^1\text{H-NMR}$ of the synthesized polymeric additives Co-1 and Co-2 (Figure 2) shows the peaks between 4.1–4.5 ppm indicate the presence of OCH_2 protons of the triglyceride moiety. Peaks in the range of 0.7–0.8 ppm indicate methyl protons, 1.15–1.95 ppm indicates methylene protons, whereas a decrease in the intensity at 5.2–5.4 ppm proves the construction of the copolymeric additives.

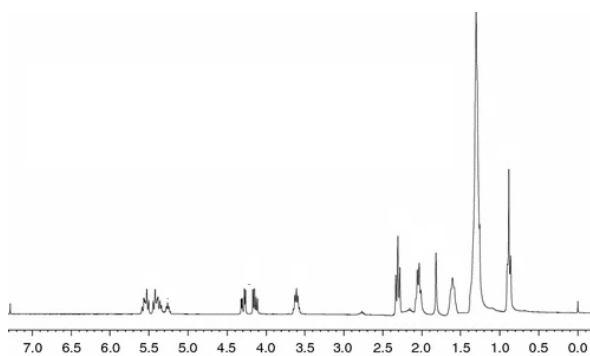


Fig. 2. $^1\text{H-NMR}$ spectra of Co-1; copolymer of castor oil and lauryl methacrylate

3.2. Thermogravimetric analysis (TGA) study

The thermal stability obtained from TGA results of the two copolymers is shown in Figure 3, where the percent weight loss (PWL) of the copolymers is plotted against increase in temperature ($^{\circ}\text{C}$). Both the copolymers show good thermal stability. The graph demonstrates that the percentage of decomposition of Co-2 is smaller than that of Co-1 at any given temperature. The percentage of weight loss for Co-1 at 300, 400, and 500 $^{\circ}\text{C}$ is 5, 10, and 55 %, respectively, while the percentage of weight loss for Co-2 at the same temperatures is 15, 20, and 75 %. As a result, it is evident that Co-1 has greater thermal stability than Co-2. This may be due to lower molecular weight of Co-2 compared to Co-1.

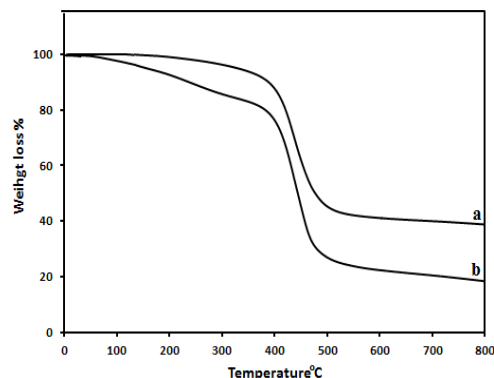


Fig. 3. TGA analysis results of Co-1 and Co-2

3.3. Molecular weight data analysis

The experimental data of weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity index (PDI) of the two additives (Co-1 and Co-2) are listed in Table 1. From the obtained results, it has been found that polydispersity index (PDI) and average molecular weight (M_w) of additive (Co-1) is higher as compared to Co-2. The results reveal that (Co-1) tend to form cross-linked polymer chains while (Co-2) consist more of linear polymer chains [17].

Table 1: Molecular weight of the prepared copolymers

Additive	M_w (g/mol)	M_n (g/mol)	PDI
Co-1	17387	11761	1.47
Co-2	10055	8409	1.22

3.4. Analysis of viscosity values

Viscosity is an essential property of a liquid that exposes the fluid's resistance to flow. The viscosity index is a number that reflects the rate at which viscosity changes as a function of temperature [18]. Viscosity index of the base oil without polymeric additives (Co-1 and Co-2), and blended oil with different concentrations of polymeric additives, ranging from 1% to 4% (w/v), are tabulated in Table 2. The results show that the values of viscosity index of the base oils mixed with additives were substantially higher than those of the base oils without additives. It may be because the base oil contains high molecular weight polymeric molecules [19]. The investigation also revealed that with an increase in polymeric additives content, the values of viscosity index increased. Besides this, the base oil blended with Co-1 has higher viscosity index value than the base oil blended with Co-2 (Figure 4). This may be due to higher molecular weight and higher crosslink density of Co-1 compared to Co-2 (Table 1). In addition, the kinematic viscosity of formulations was determined at temperatures ranging from 40 to

100 °C. For both additives, when the temperature was elevated to 100 °C, a simultaneous drop in viscosity was noticed, as shown in Table 2. Viscosity can decrease when temperature rises because the thermal kinetic energy of the molecules increases, resulting in a lower internal resistance to flow and reduced viscosity [20].

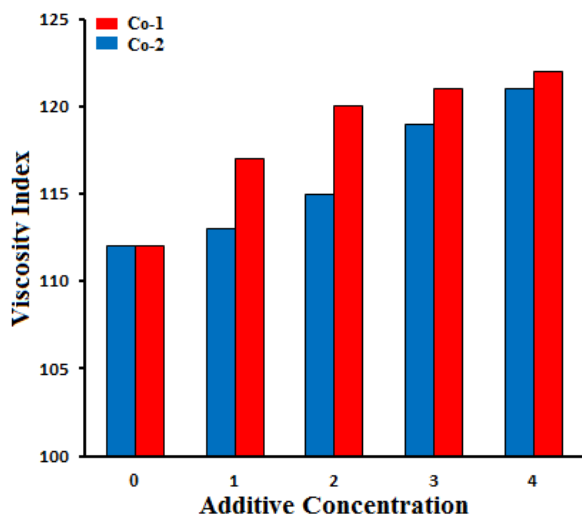


Fig. 4. Viscosity index variation of the base oil blended with different concentrations of additives.

3.5. Analysis of Pour point values

The fluidity of the oil was determined under the lowest temperature condition by using ASTM D-97 pour point method. Values of pour point and cloud point temperatures are tabulated in Table 2. Both the copolymeric additives (Co-1 and Co-2) were tested for their ability to lower the pour point (Figure 5). In addition, Co-1 additive on the formulation in lubricant oil at various concentrations, i.e. 1%, 2%, 3% and 4% (w/v) shows a pour point value as -11, -12, -15 and -15 °C respectively while pour point values for Co-2 additive on the formulation in the

same concentrations as previously discussed are -12, -14, -15 and -15 °C, respectively. Since the base oil's pour point was reported as -10 °C, a substantial drop in pour point was observed after adding both copolymers to the base oil. It is clearly observed that as the concentration of copolymers in the base oils increased, the efficiency as a pour point depressant gradually improved. However, the improved pour point depressant qualities are related to the disruption of the stiff network of wax crystals that develop at lower temperatures from the dissolved waxy hydrocarbons in mineral oils [21]. Pour point depressants minimize growth the size of wax crystals, reducing their ability to flocculate and interlock with one another. Pour point depressants normally contain a wax-like paraffinic component that cocrystallizes with the oil's wax-forming components and effectively becomes a part of them and the polar component present in the pour point depressants limits their degree of cocrystallization [22].

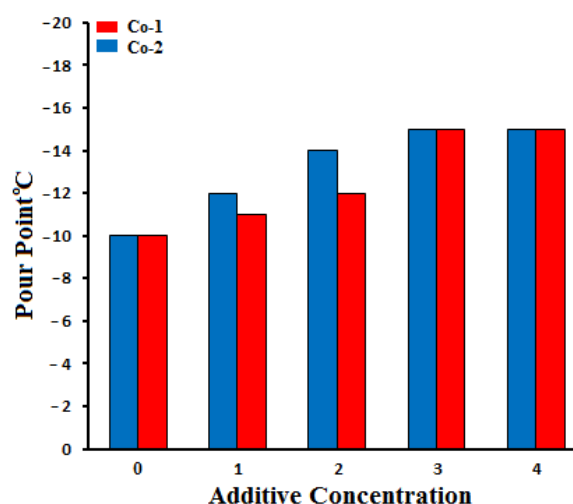


Fig. 5. Pour point variation of the base oil blended with different concentrations of additives.

Table 2: Performance properties of base oil and its mixtures with different concentrations of additives

Performance Properties	Base Oil	Co-1 additive				Co-2 additive			
		1.0%	2.0%	3.0%	4.0%	1.0%	2.0%	3.0%	4.0%
Viscosity at 40 °C	28.11	32.55	33.65	34.98	34.54	29.66	30.40	32.82	33.41
Viscosity at 100 °C	4.378	5.112	6.212	7.447	7.319	4.091	4.688	6.101	6.322
Viscosity Index	112	117	120	121	122	113	115	119	121
Pour Point (°C)	-10	-11	-12	-15	-15	-12	-14	-15	-15
Cloud Point (°C)	-6	-9	-11	-11	-12	-7	-10	-13	-13

4. Conclusions

In this research, detailed analyses of the prepared copolymers, castor and corn oils with lauryl methacrylate, were carried out to evaluate their performance as a multifunctional additives. Castor oil copolymer is thermally more stable than corn oil copolymer, according to thermal gravimetric analysis. The findings showed that adding these additives to the base oil significantly improved their lubricant properties. Copolymer of castor oil was better viscosity index improver, whereas the copolymers of corn oil found to be most effective as pour point depressants.

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