



Synthesis of behenyl acrylate and citral based polymers: A comparative study on their performances as biodegradable multifunctional lube oil additives

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Abstract

Vegetable oil based biodegradable polymeric additives have attracted much attention keeping in view the increasing environmental concern. In the present context homopolymer of behenyl acrylate, and its different copolymers with varied percentages of Citral have been synthesised via free radical polymerisation. All the prepared polymers were characterised by FT-IR and NMR spectroscopy and their molecular weights were measured by GPC. Their performances as pour point depressant (PPD) and viscosity index improver (VII) in lube oil have been evaluated. Thermo Gravimetric Analysis (TGA) of these polymers accounted for their thermal stability as a polymeric additive. Also eco-friendly nature of the Citral based polymers was established via biodegradability test. The results have successfully sought for the establishment of a potential candidate towards application of greener additives in automotive industry.

Keywords: Polymeric additive; behenyl acrylate; pour point depressant; viscosity index improver; thermo gravimetric analysis

Introduction

Modern lubricants consist of the base oil as a major constituent along with some additives required for providing some specific characteristics or sometimes enhancing the existing properties.¹ Antioxidants, detergents, dispersants, corrosion inhibitors, viscosity index improvers (VIIs), pour point depressants (PPDs), antiwear and antifriction additives are some of the important types of these additives. Out of these, VIIs and PPDs are added in the large quantities because the viscosity and fluidity variation with temperature determines the applicability of a lubricant formulation in low and high temperature operational conditions with effective and efficient performance.² Utilisation of polymeric additives as chemical treatment is considered as the most valuable and economic method to inhibit the wax precipitation at low temperature. Usually polymeric additives contain non polar long hydrocarbon chain of 14 to 25 carbon atoms along with a polar segment typically acrylates or acetates.^{3,4} It is the polar head group which is responsible for the modification of wax crystals morphology whereas the non-polar long hydrocarbon chain is responsible for the interaction between the additives and paraffin.

Several polymeric additives have been created and utilized as PPDs, especially linear polymers of alkyl acrylate or methacrylate having a pendent alkyl side chain of specific length have been extensively used as flow improvers (FIs) or pour point depressants (PPDs).⁵⁻¹¹ The function of PPDs has already been discussed in our previous works where it is clearly mentioned that PPDs co-crystallize along with the wax species present in the oil at lower temperature and modify the growing pattern of wax crystal structures.¹³ Recently a considerable number of studies has been reported on the structure-reactivity relationship for the polymers of higher alkyl acrylates and methacrylates.^{12,13} These studies invoked the research towards modified processes for the polymerization of *n*-alkyl acrylates with narrow molecular weight distribution (MWD).¹⁴

Various polymeric additives are available commercially such as poly (ethylene-co-vinyl acetate) (EVA),¹⁵ poly(ethylene-butene) (PEB),¹⁶ polymethacrylates¹⁷ and modified maleic anhydride copolymers.⁴ Number of studies have been reported on versatile application of these additives including polyacrylate polymers with polar building blocks as wax modifier¹⁸, linear polymer or copolymer having pendant hydrocarbon chains as flow improvers¹⁹ and again some studies also investigated the effect of molecular weight (MW) and molecular weight distribution (MWD) on the performance of these additives.²⁰

Homopolymers of alkyl acrylates and methacrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour point depressants and flow improvers in high waxy crude oils, lubricating oils and fuel oils. The alkyl chain length in these polymers is usually more than 14 carbons. Behenyl acrylate (BA) consists of a mixture of C₂₂, C₂₀ and C₁₈acrylates and is used extensively in the preparation of these additives.¹³ Recently development of the novel

additives based on copolymers containing n-alkyl acrylates has gained huge attention due to their multifunctional nature and the fact that the comb shaped polymeric additives can be more effective as PPD in lube oil by providing different nucleation sites for the precipitation of wax.²¹ Dao in 2017 has reported that copolymers formed by stearyl methacrylate and behenyl acrylate with vinyl acetate using AIBN as initiator give high efficiency to reduce pour point temperature.²² R. K. Singh et al. have reported the successful synthesis, characterization, and performance evaluation of two homopolymers of C₁₈ alkyl acrylate and N,N-dimethylacrylamide and their three copolymers as synthesized by using 1:1, 1:2, and 2:1 monomer ratios as VII and PPDs in polyol base oil taking the homopolymers as reference.² B. Subrahmanyam et al. had presented a thorough study on the effect of initiator concentration and monomer concentration on the molecular weight and molecular weight distribution in behenyl acrylate polymerization. They found that at higher concentration of initiator and monomer, the branching reactions led to gel formation in behenyl acrylate polymerization. They reported that viscosity of the polymerizing medium also influenced the high conversion polymerization in alkyl acrylate polymerization.¹³

Thus growing demand for requirement of high performance characteristics and increasing environment related concerns have forced the researchers to develop new multifunctional polymeric additives so that maximum activity can be achieved with minimum dosage. Citral (3,7-dimethyl-2,6-octadienal) is basically a monoterpenoid. It is a yellow coloured flavonoid found in lemongrass oil having characteristic lemon like odor. It has been explored for plenty of biological activities especially as antifungal agent.²³ It contains huge percentage of active unsaturation with polar functional groups and thus is very much prone towards effective polymerization and also efficient for enhancement of lubricant performances (pour point, antiwear). Recent study from our lab with citral²⁴ has provoked its further exploration towards development of biodegradable polymeric additive. Here we have prepared homopolymers of behenyl acrylate and further its copolymers with Citral at variable percentages. All the prepared polymers have been characterised by FT-IR and NMR spectroscopy. Their thermal stability and molecular weight were determined and then they were evaluated as VII and PPD in lube oil. Further their Thermo gravimetric analysis and biodegradability test were also performed.

Materials and Methods

Materials

Behenyl alcohol (Merck Specialties Pvt. Ltd.), acrylic acid (Merck Specialties Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), Hexane (99.5%, S. d Fine Cheme Ltd.) and Methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and Benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. The properties of the used base oils are tabulated in Table 1. Citral (95% pure) was bought from SRL Pvt. Ltd.

Table 1: Base Oil (BO) Properties

Physical Property	BO1	BO2
Density (gcm ⁻³ at 40 °C)	0.837	0.868
Viscosity at 40 °C in cSt	7.136	23.392
Viscosity at 100 °C in cSt	1.856	3.915
Pour Point (PP in °C)	-3	-6
Cloud Point (°C)	-10	-8

BO1, BO2 collected from IOCL, Dhakuria, West Bengal

Preparation of esters

The ester (Behenylacrylate, BA) was prepared by reacting 1.1 mol of acrylic acid with 1 mol of behenyl alcohol. The reactants were mixed with toluene along with few drops of concentrated sulphuric acid as a catalyst, 0.25 % hydroquinone with respect to the total reactants as polymerization inhibitor in a resin kettle and heated gradually from room temperature to 403K using a well-controlled thermostat under a slow stream of deoxygenated nitrogen. The whole process was carried out in reflux condition. The extent of esterification was monitored by the amount of liberated water.

Purification of prepared esters

The prepared ester was refluxed for 3 hours with suitable amount of charcoal and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separatory funnel several times to ensure complete removal of untreated acid. The ester was then washed repeatedly with distilled water to remove any traces of sodium hydroxide. The purified ester was then left overnight on calcium chloride. It was then removed by distillation under reduced pressure. Then the ester was ready to be used in the polymerization process.

Preparation and purification of the polymers

The polymers (homo and copolymers) were prepared by free radical polymerization at different percentage composition of monomers (table 2) in presence of BZP as initiator (0.5% w/w, with respect to the total monomer). The polymerisation process was carried out in a four-necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of deoxygenated nitrogen at 90°C for 6 h. At the end of the reaction time, the

reaction mixture was poured into methanol to terminate the polymerization process and precipitate the polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40°C.

Measurements

Molecular weight determination

With the help of Gel Permeation Chromatography (GPC, Water 2414, polystyrene calibration), the number average molecular weight (M_n) and weight average molecular weight (M_w) of the prepared polymers were measured in HPLC grade THF (0.4%, w/v) at 308 K temperature at a flow rate of 1 mL/min. The values are given in Table 2.

Spectroscopic Measurements

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

Performance evaluation as pour point depressants in base oil

The effect of additive concentration on pour point of two base oils (BO1 and BO2) was tested by using different doping concentrations ranging from 1% to 6% (% w/w) for each of the prepared polymers. According to the ASTM D 97-09 method the pour points of the prepared solutions were measured using cloud and pour point tester model WIL-471 (India) given in Table 3 & 4.

Performance evaluation as viscosity index improver (VII)

Viscometric parameters were determined according to ASTM D 2270-10. The kinematic viscosity of the base oils containing the polymers determined at 313 and 373 K. Different concentrations of the polymers in the base oil (% w/w) from 1% to 6% were used to study the effect of concentration on VI of the additive-doped lube oil. All of the experimental data given in Table 5 & 6 were noted by taking an average of three experimental results under identical conditions in each case.

Determination of thermo gravimetric analysis (TGA) data

TGA data (Table 7) was measured on Mettler TA-3000 system, at a heating rate of 10K min^{-1} . The variation of temperature within the range was $\pm 10\text{K}$ during the experiment. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.5\%$.

Biodegradability test

To evaluate biodegradability of the prepared polymers, Soil Burial Test (SBT) method was utilized as per ISO 846:1997 standard²⁵ using the soil sample collected from North Bengal University campus with pH 7.2 and 25% moisture. Percentage weight loss (PWL) of the polymer samples after a definite interval of times was calculated to determine the extent of degradation. The results were verified by IR spectroscopy and molecular weight determination by GPC method. For Soil Burial Test (SBT), separate films containing about 2.0 g of different samples were buried in the soil which were then incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30°C with relative humidity of 60% for 3 months and thus subjected to the action of microorganisms present in the soil. After each regular interval of 15 days, the soil sample is taken out and the polymer sample was recovered from it by dissolving in chloroform, filtered, dried and percentage of decomposition was measured. The detailed experimental procedure followed is mentioned in our previous work.²⁶

Results and discussion

Molecular Weight Analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity index data (PDI) of the prepared polymers are given in Table 2. Analysing the experimental data, it was found that the homopolymer of behenyl acrylate (P_1) had higher number average and weight average molecular weight than the others. Since it is a homopolymer of C_{25} monomer, it is obvious that its molecular weight is higher compared to the copolymers where Citral was incorporated. Again in terms of polydispersity index (PDI) P_4 polymer is least poly-dispersed which indicates better uniformity. With increasing concentration of Citral, the polymers (P_2 , P_3 & P_4) exhibited higher molecular weight and lesser polydispersity index.

Table 2: Weight percentage (%) composition, M_n , M_w and PDI values of polymers (P₁ to P₈)

Polymer	% of BA	% of Citral	M_n	M_w	PDI
P ₁	100	–	38563	53217	1.38
P ₂	98	2	28832	38347	1.33
P ₃	96	4	28510	35067	1.23
P ₄	94	6	29567	33115	1.12

BA = Behenyl acrylate, M_n = Number average molecular weight, M_w = Weight average molecular weight, PDI = Polydispersity index

Spectroscopic analysis

In FT–IR spectroscopy almost all the polymers being acrylate produced similar spectra. Peaks around 1732–1735 cm^{-1} clearly indicated the presence of ester carbonyl group in each case. Strong peak at around 1695 cm^{-1} corresponding to conjugated aldehydic C=O group accounted for successful incorporation of citral while copolymerization. In general any alkenyl C–H stretching produces IR peak at about 3100 cm^{-1} , but here in the homopolymers no corresponding peak has been obtained. This observation supported complete and successful homopolymerisation. But in case of the copolymers medium peak around 1610 cm^{-1} accounted for the conjugated C=C group.

In ^1H NMR spectra peaks appeared in the range of 3.94–4.12 ppm clearly indicated the presence of $-\text{OCH}_2-$ protons. The absence of peaks around 6 ppm indicated absence of C=C unsaturation and hence supported total polymerisation in case of the homopolymer. Again peaks around 9.68 ppm indicated presence of aldehydic C–H group in the copolymers which further accounted for successful incorporation of citral while copolymerization. In ^{13}C NMR spectra, peaks at 176–178 ppm indicated the presence of ester carbonyl carbon. The peaks at 64.67–66.06 ppm corresponded to the $-\text{OCH}_2-$ carbons, peaks ranging from 13.09–44.66 ppm for all other sp^3 carbons. Again no peak in the range of 120–150 ppm indicated the absence of sp^2 carbons and confirmed the polymerization in the homopolymer. In the copolymers peaks around 190 ppm accounted for the aldehyde group of citral.

Performance evaluation as pour point depressant

The pour point data given in Table 3 & 4 clearly prove that the prepared polymers are good pour point depressants for both the base oils. In case of the homopolymer (P₁), with increasing concentration its effectiveness as PPD decreases. Very high molecular weight of this polymer might be the reason for its low solubility at higher concentration in both the base oils. But the copolymers have been proved to be better PPDs in both the base oils. Comparing all the pour point data, it can be said that the copolymer of 94% behenyl acrylate and 6% citral (P₄) gave the best result. Almost in all the cases the pour point depression curves get flattened above 4% concentration since at higher concentration the polymers suffer lower solubility and hence their effectiveness as PPD also diminishes.

Table 3: Pour point ($^{\circ}\text{C}$) data with respect to the different concentrations of the additives in BO1

Additive	1%	2%	3%	4%	5%	6%
P ₁	–13.3	–13.6	–12.9	–12.7	–12.3	–11.8
P ₂	–16.0	–16.5	–17.2	–17.8	–18.1	–18.0
P ₃	–18.1	–18.6	–19.2	–19.4	–19.4	–19.1
P ₄	–20.9	–21.2	–21.6	–22.1	–22.0	–22.0

Concⁿ represents concentration in % w/w

Table 4: Pour point ($^{\circ}\text{C}$) data with respect to the different concentrations of the additives in BO2

Additive	1%	2%	3%	4%	5%	6%
P ₁	–20.4	–20.3	–19.4	–18.8	–18.1	–17.6
P ₂	–25.5	–25.8	–26.1	–26.4	–26.2	–26.2
P ₃	–26.4	–26.9	–27.2	–27.6	–27.6	–27.3
P ₄	–28.6	–29.1	–29.4	–29.8	–30.2	–30.2

Concⁿ represents concentration in % w/w

Performance evaluation as viscosity index improver

Solubility of the polymer, its molecular weight and composition play important role on its performance as viscosity index improver.²⁷ It is said that polymers exist as random coils in base oil solutions. As the temperature increases solubility of the polymer increases and it unfolds itself to an open configuration of higher volume and hence overall higher viscosity is exhibited at higher temperature by polymer-doped base oil. This activity offsets the normal trend of decrease in viscosity with increase in temperature.²⁸

It is seen from the Table 5 & 6 that all the prepared polymers are effective viscosity index improvers for both the base oils. Here again due to very high molecular weight and hence lower solubility, the homopolymer of behenyl acrylate (P₁) is least effective as VII among all. On the other hand, the copolymer of behenyl acrylate and 6% citral (P₄) has been proved to be the best viscosity index improver in both the base oils. The rests are almost comparable VIIs. With increasing concentration of the polymer in the base oil, total volume of the polymer micelle increases and hence the viscosity index data also increases.²⁹

Table 5: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO1

Additive	0%	1%	2%	3%	4%	5%	6%
P ₁	85	97	98	100	101	103	102
P ₂	85	98	99	101	104	114	118
P ₃	85	100	102	103	106	117	120
P ₄	85	110	112	113	115	120	122

Concⁿ represents concentration in % w/w

Table 6: Viscosity Index (VI) data with respect to the different concentrations of the additives in BO2

Additive	0%	1%	2%	3%	4%	5%	6%
P ₁	80	102	104	107	109	115	119
P ₂	80	104	105	106	109	116	119
P ₃	80	105	106	108	110	118	120
P ₄	80	120	121	123	125	130	132

Concⁿ represents concentration in % w/w

Analysis of TGA data

The thermal studies confirmed that all the prepared polymers are thermally stable (Table 7). Lower the percent weight loss (PWL) higher will be the thermal stability. Therefore, among the prepared polymers, the copolymer of behenyl acrylate and 2% citral (P₂) is thermally most stable while the homopolymer of behenyl acrylate (P₁) is thermally least stable. Higher thermal stability of the additives indicated their suitability as lubricant additives.

Table 7: TGA data of the polymers

Polymer	Decomposition temperature	Percent weight loss (PWL)
P ₁	250/340	23/86
P ₂	250/360	12/82
P ₃	260/380	14/85
P ₄	250/380	13/80

Analysis of biodegradability test results

From the results obtained from biodegradable test (Table 8) it was found that the degradation of the recovered samples taken every 15 days interval increases with increasing time. The copolymer of behenyl acrylate and 6% citral (P₄) showed highest degradation and after 90 days' span the recovered sample showed over 40% weight loss followed by P₃ (over 37% weight loss) and P₂. Among the four polymers, the homopolymer P₁ showed least biodegradation and after 90 days' span the recovered sample showed no weight loss at all. Therefore, the lube oil additives prepared from citral exhibited significant biodegradation.

Table 8: Results of biodegradability test by soil burial test for polymeric additives

Soil burial test	
Polymers	Microorganism Wt. loss (%)
P-1	00
P-2	31.60
P-3	37.70
P-4	40.30

Conclusions

All the prepared polymers have been evaluated as effective multifunctional and thermally stable additives for lube oil. In terms of molecular weight the homopolymer of behenyl acrylate exhibited highest number average and weight average molecular weight. Again the PDI value accounts for better uniformity in the copolymers. But the homopolymer is very much less effective as PPD as well as VII which may be attributed to its solubility problem. All the other polymers have been proved to be good flow improvers in both the base oils. Especially the copolymer of behenyl acrylate and 6% citral resulted highest depression in pour point in both cases. This polymer was also proved to be the best VII among all the prepared ones. Furthermore the citral based polymers were proved to be biodegradable also which accounted for their eco-friendly nature. However citral based some other polymeric additives should also be evaluated and much more properties like shear stability must be explored before its establishment as a potential biobased polymeric additive.

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