Evaluation and Synthesis of Environmentally Benign multifunctional additives for lube oil

ABSTRACT

Behenyl acrylate (BA) homo-polymer and its copolymers with citral were synthesized with varying percentage compositions (w/w) and subjected to thorough characterization throughGPC (gel permeation chromatography)analysis and spectroscopic techniques (FT-IR, NMR). The polymers' capability was assessed through viscosity index improvers/viscosity modifiers (VII or VM), antiwear (AW) additives and pour point depressants (PPD) for base oils (lubricating oil). The action mechanism of the PPD properties was investigated through photomicrographic analysis. Additionally, the polymers'thermal stability was measured using TGA or thermo gravimetric analysis. Biodegradability tests on copolymers were conducted using soil burial test (SBT)andthe Disc Diffusion (DD) method. The copolymers exhibited exceptional PPD, VII, and AW performance when incorporated into lubricating oil.

Keywords: Citral, Copolymer, Biodegradable, Lube oil, Viscosity index improver, Pour point Depressant, Antiwear, Photo micrographic analysis.

1. Introduction

Lubricants consist of a combination of a base fluid and additives designed to enhance performance. The additive content typically ranges from 1% to 30% or even higher. While mineral oils of petroleum origin are commonly used as base fluids, vegetable and synthetic oils also find application. Polymeric additives are introduced to the base fluid to improve the operational efficiency of engine oil and extend the engine's lifespan.

Additives typically serve various functions, such as ameliorating the pour point (PP) [1] of base oils through the dissolution of wax crystal deposits [2] at lower temperatures, boosting the viscosity index (VI) [3] to maintain viscosity stability amidst temperature fluctuations, minimizing wear, and effectively transporting contaminants away.These components are commonly labeled as viscosity index improvers (VII) [5],pour point depressants (PPD) [4], detergent-dispersants [7] and antiwear agents [6].

Commercially available synthetic acrylate-based additives, although effective, are non-biodegradable, prompting environmental concerns. The increasing desire for environmentally friendly technology has spurred researchers to create lubricant additives that are ecologically benign.Vegetable oils [8-11], recognized for their natural occurrence, biodegradability, non-toxicity, and high viscosity index, present a promising alternative [12]. They exhibit excellent tribological properties, acting as antiwear and friction modifiers in lubricant formulations [13, 14].

Modified vegetable oils have been utilized as additives in lubricating oils in numerous cases, with patents describing their application as extreme pressure additives, friction modifiers, and viscosity index improvers [15-17]. In line with these considerations and as part of our ongoing efforts to develop chemical additives for lubricating oil, our present investigation focuses on synthesizing copolymers of acrylate ester based citral through copolymerization. The aim is achieving an optimal balance between performance and environmentally friendly chemistry. The study encompasses the synthesis and characterization of behenyl acrylate (BA) homopolymer and BA copolymer with citral, followed by biodegradability testing and evaluation of their effectiveness as pour point depressants, viscosity modifiers, and antiwear additives.

2. Material and methods

2.1 Materials

Hydroquinone, sulfuric acid and Toluene, were sourced from Merck Specialities Pvt. Ltd. Acrylic Acid (stabilized with 0.02% Hydroquinone monomethylether), Behenyl alcohol and n-Hexane were procured from SRL Pvt. Ltd. Methanol and Benzoyl Peroxide (BZP) wereobtained from Thomas Baker (Chemicals) Pvt. Ltd. andLOBA chemicals respectively.They underwent recrystallization using a $CHCl_3$-MeOH mixture before application. Citral was sourced from a nearby grocery store, and the base oils were acquired from IOCL (Indian Oil Corporation Ltd.), Kolkata, India. Remaining substances were utilized in their pristine condition without extra purification. All specimens were subjected to testing before reaching their designated expiration dates.

3. Methods

The thermal radical polymerization of behenyl acrylate and its subsequent copolymerization with citral at varying concentrations (5%, 10%, and 15% w/w) were carried out employing benzoyl peroxide (BZP) as the initiator. The resulting additives were subjected to thorough characterization using spectral analysis techniques, including Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR). The determination of the average molecular weight of the polymeric additives, both number average (Mn) and weight average (Mw), was accomplished using gel permeation chromatography (GPC). Tetrahydrofuran (THF) of high-performance liquid chromatography (HPLC) grade served as the mobile phase in the water GPC system, calibrated with polystyrene, and the analysis was conducted at 40°C.

The thermal stability of the additives was evaluated using the Mettler TA-3000 system, employing a heating rate of 10 K min^{-1}. The multifunctional performance of the base oil treated with additives, encompassing improvements in viscosity index, pour point depression, and antiwear properties, was assessed in accordance with ASTM methods. The antiwear (AW) characteristics were determined utilizing a Four-ball wear test apparatus, following the ASTM D 4172-94 method [18], with a weld load of 392 N at 75°C for 30 minutes and a rotational speed of 1200 rpm.

The biodegradability of the polymeric additives underwent testing through the disc diffusion method [19], evaluating their effectiveness against fungal pathogens, and the soil burial test as per ISO 846:1997 [20, 21]. Microbial degradation was confirmed by measuring the shift in the infrared (IR) frequency of the ester carbonyl after the biodegradability test.

4. Results and discussion

4.1. Spectroscopic description

In FT-IR spectrum, homopolymer of behenyl acrylate (P-1) demonstrated an absorption peak at 1732 cm^{-1}, corresponding to ester carbonyl, attached with distinctive peaks at 1467, 1271, 1190, and 1060 cm^{-1}. The ^{1}H NMR spectra of HP-1 revealed a broad singlet centered at 4.02 ppm, associated with the –OCH$_2$ protons. Methyl protons from the behenyl chain were evident between 0.81 ppm and 0.86 ppm, and the lack of a singlet in the 5-6 ppm range indicated the absence of vinylic protons in the polymer. The ^{13}C NMR spectrum of P-1 disclosed the carbonyl carbon at 174.4 ppm, along with other SP^3 carbons ranging from 65.03 to 10.66 ppm.

In FT-IR spectrum of the copolymers, the ester carbonyl peak appeared at 1731 cm^{-1}, containing a peak at 1738 cm^{-1} corresponding to the citral's aldehydic group. The ^{1}H NMR of copolymers exhibited a multiplet in the span of 4.119-4.402 ppm, indicating –OCH$_2$ protons. SP^3 protons were observed within 1.259-1.989 ppm, while peaks at 5.343 ppm and 5.360 ppm were attributed to ethylenic unsaturationfromcitralportion of copolymer. One peak around 10 ppm indicated presence of the aldehydic hydrogen of citral in that copolymer. In^{13}C NMR of the copolymer, peaks within 167.70-173.36 ppm indicated the ester carbonyl carbon.Peaks at 190.81 ppm were due to the aldehydic carbonyl group of citral. The –OCH$_2$ carbon peak appeared at 68.93 ppm. Peaks within 14.09-34.05 ppm represented all SP^3 carbons of the copolymer.

4.2 Performance of the prepared additives in the form of pour point depressant

The results of samples' pour point depressants (PPDs), covering a range of additive concentrations within 1 wt% to 5 wt%, are outlined in Table 1. The data vividly demonstrates the efficacy of the prepared additives as pour point depressants, showcasing a consistent reduction in pour point with increasing additive concentration. Notably, the pour point magnitudes of copolymers (P-2, P-3, and P-4) exhibit a remarkable similarity and consistently register lower values compared to the homopolymer (P-1). Consequently, all copolymers demonstrate exceptional pour point depressant properties.

Table-1: Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

PPD in BO1 Concentration of additives, % in w/w								PPD in BO2 Concentration of additives, % in w/w					
Sample	0	1	2	3	4	5		0	1	2	3	4	5
P-1	-3	-12	-15	-15	-15	-13		-6	-12	-15	-16	-16	-14
P-2	-3	-12	-18	-21	-24	-28		-6	-15	-17	-25	-28	-28
P-3	-3	-12	-17	-24	-27	-30		-6	-18	-21	-27	-30	-32
P-4	-3	-11	-15	-22	-26	-28		-6	-16	-21	-27	-29	-30

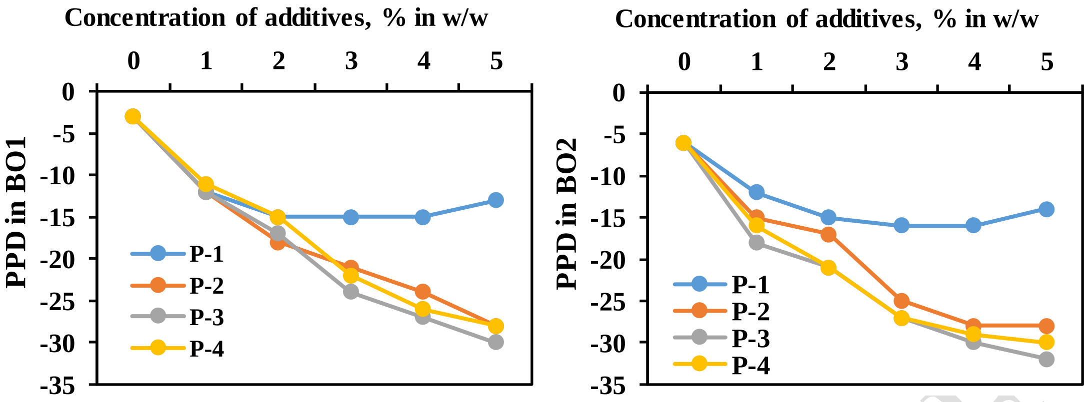

Figure 1:Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

The efficacy of the polymers as potent pour point depressants was evaluated through photomicrographic experimentation. The wax crystal size exhibited a notable reduction, transitioning from a large crystal structure in the base oil to very small dots dispersed in the oil phase of the lubricating oil [22].

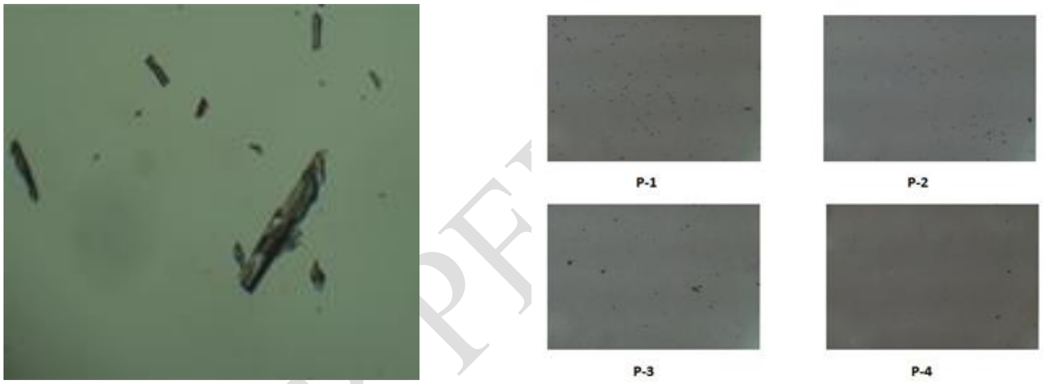

Figure 2:Photomicrographic images of base oil(left side) and additive (P-1, P-2, P-3 and P-4) Doped base oil (right side)

4.3. Performance of the prepared additives as viscosity index improver(VII)

Table 2 presents the viscosity indexes for base oils treated with additives derived from polymers (P-1, P-2, P-3, and P-4). The data reveals a steady increase in VI magnitudes as the polymer concentration rises in both base oil types (BO1 and BO2), reaching a peak at 4%. The elevated polymer concentration corresponds to an increased volume of polymer micelles within the oil solutions. Consequently, a higher concentration of the polymer contributes to a higher VI, in contrast to a lower concentration of the same polymer. **The VIscorresponding to additive-doped base oils are summarized in Table 2.**

Table 2.VIs corresponding to additive-doped base oils

	VI in BO1 Concentration of additives, % in w/w						VI in BO2 Concentration of additives, % in w/w					
Sample	0	1	2	3	4	5	0	1	2	3	4	5

P-1	80	110	112	114	118	121	89	109	112	119	121	122
P-2	80	113	116	119	119	127	89	114	118	121	122	122
P-3	80	121	126	131	135	141	89	115	126	129	133	137
P-4	80	119	121	123	127	134	89	116	122	122	124	128

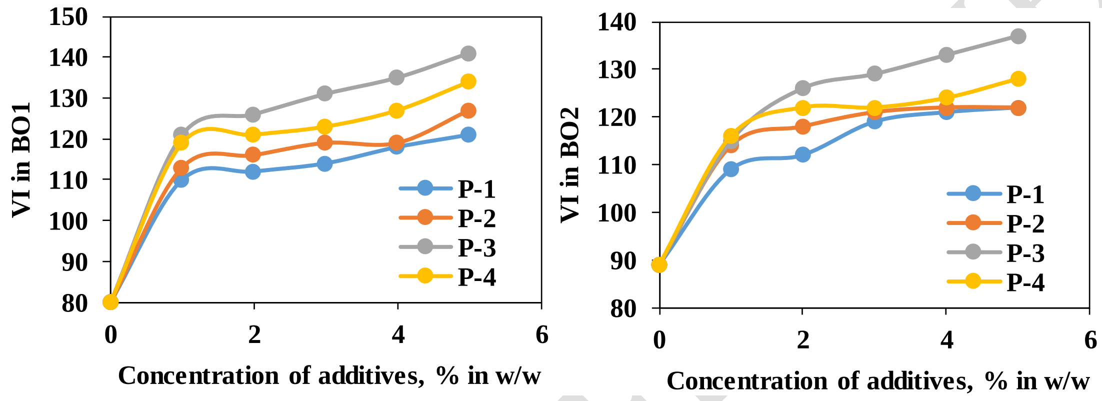

Figure 3:The VIs corresponding to additive-doped base oils

4.4 Performance of the prepared additives as antiwearadditive

A reduction in wear scar diameter (WSD in mm) was observed with increasing additive concentration in the case of studied base stocks with varying load conditions. The most distinct drop was observed at 20 kg load condition, as illustrated in figures 2 and 3. This suggests that the additives exhibited comparatively lesser effectiveness at higher load conditions. However, there was no noteworthy enhancement in the performance beyond a 5% additive concentration.

It was observed that the studied copolymers exhibited superior antiwear properties compared to the homopolymer (P-1). The presence of aldehydic functionality and ester functionality can be attributed to such observation[23,24]. As a result, copolymer (P-4), with larger fraction of citral units, demonstrated enhanced antiwearperformance.

Table 3:Antiwearvalues of polymers P-1, P-2, P-3 and P-4 in the base oils(BO1 and BO2) at 40 kg load

	VI in BO1 Concentration of the additives, % in w/w						VI in BO2 Concentration of the additives, % in w/w					
Sample	0	1	2	3	4	5	0	1	2	3	4	5
	1.067	0.991	0.887	0.718	0.713	0.665	1.110	0.984	0.907	0.865	0.844	0.823

P-1												
P-2	1.067	0.954	0.861	0.711	0.688	0.645	1.110	0.971	0.891	0.843	0.821	0.812
P-3	1.067	0.901	0.813	0.703	0.641	0.633	1.110	0.898	0.822	0.804	0.791	0.776
P-4	1.067	0.903	0.811	0.710	0.632	0.635	1.110	0.846	0.798	0.806	0.793	0.781

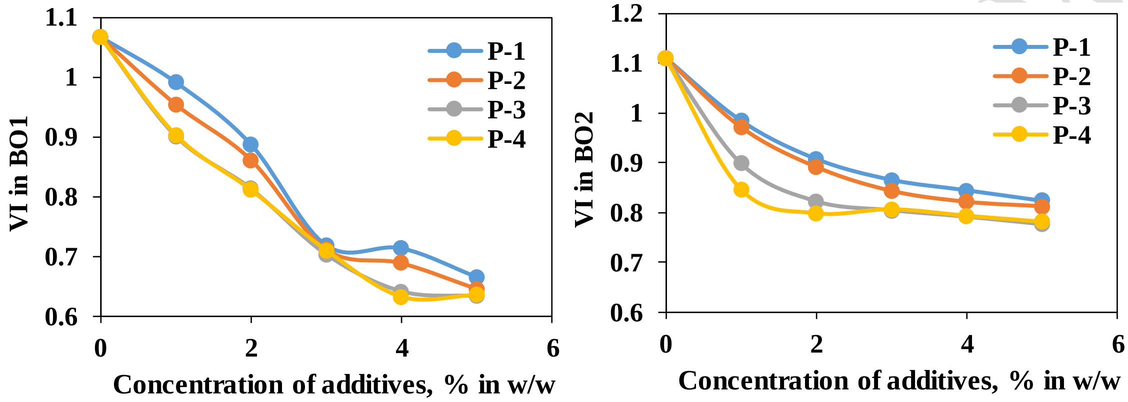

Figure 4:Antiwearvalues of polymers P-1, P-2, P-3 and P-4 in the base oils(BO1 and BO2) at 40 kg load

4.5 Analysis of biodegradability test result

The biodegradability test results obtainedfrom disc diffusion method and soil burial test (Table 4) indicates notable biodegradability for fungal pathogen Alternariaalternata, compared tothe homopolymers. This observation was substantiated by the shift in the IR frequency of the ester carbonyl. As anticipated, the copolymer exhibited superior biodegradability in comparison to the homopolymer.

Table 4 Results of biodegradability test by disc diffusion method and soil burial test for polymeric additives

Disc diffusion method		*Soil burial test*
Polymers	*Alternariaalternata* Wt. loss(%)	Microorganism Wt. loss(%)
P-1	00	00
P-2	31.60	16.30
P-3	37.70	23.20
P-4	40.30	25.70

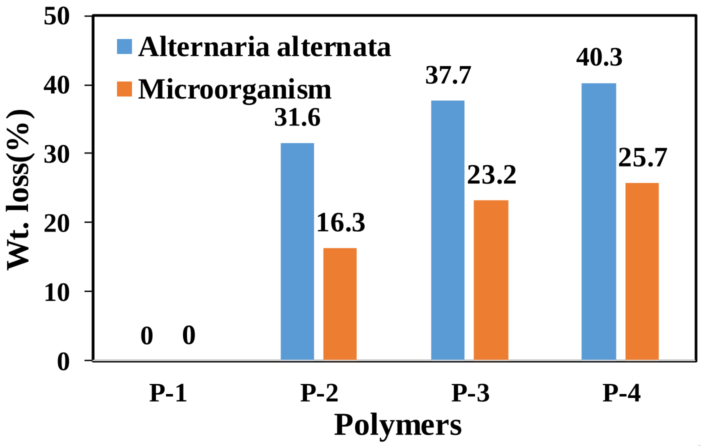

Figure 5:biodegradability test by disc diffusion method and soil burial test for polymeric additives

4.6 Determination of Molecular weight of the polymers

Table 5:Molecular weight characteristics of the polymers

Polymer sample	M_W	M_n	*PDI*
P-1	33789	38412	1.14
P-2	31854	37407	1.17
P-3	25118	30574	1.22
P-4	24272	29872	1.23

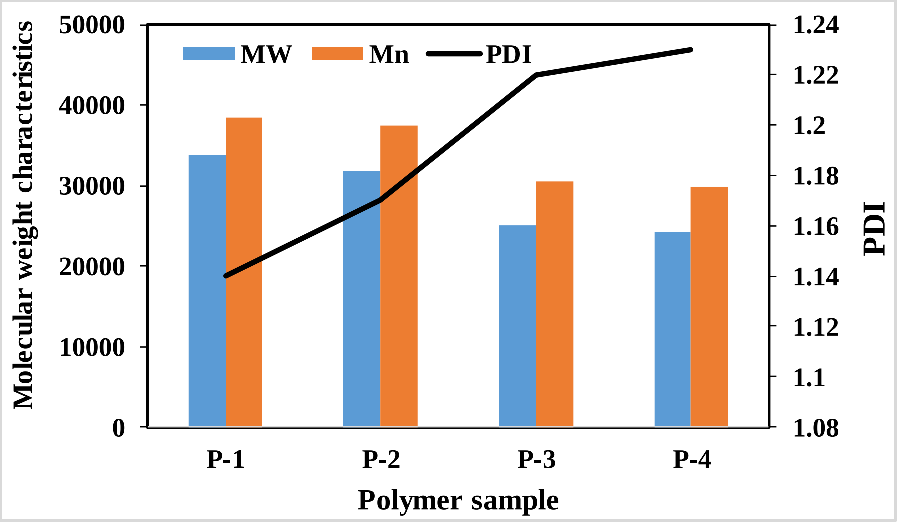

Figure 6: Molecular weight characteristics of the polymers

4.7 TGA data of all the polymer samples

Table-6 displays the Thermogravimetric Analysis (TGA) data for both the homopolymer and copolymer of dodecyl acrylate. The data reveals that the copolymers (P-2, P-3, and P-4) exhibit greater thermal stability compared to the homopolymer (P-1). Furthermore, there is a discernible trend indicating that as the concentration of citral in the feed increases, the thermal stability of the copolymers also increases.

Table6: TGA data for homo and copolymer of behenylacrylate

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
P-1	513	84
	541	77
	562	16
	589	4
P-2	523	86
	551	80
	577	21
	611	5
P-3	561	85
	584	79
	605	23
	627	8
P-4	566	85
	589	80
	617	7
	640	5

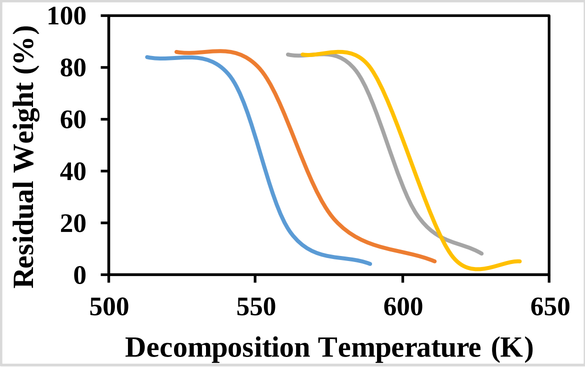

Figure 7: TGA data for homo and copolymer of behenylacrylate

4.7 Physical properties of Base oils

Table 7. Physical properties of Base oils

Properties	*BO1*	*BO2*
Density(kg.m^{-3}) at 313K	839.98	918.68
Viscosity at 313K	5.97×10^{-6}	20.31×10^{-6}
Viscosity at 373K	1.48×10^{-6}	3.25×10^{-6}
Viscosity index	80.05	89.02
Cloud point (°C)	-10	-8
Pour point (°C)	-3	-6

5. Conclusions

All the copolymers (P-2, P-3, and P-4) along with the homopolymer (P-1) demonstrated exceptional pour point depressant (PPD) and antiwear (AW) properties. Additionally, the copolymer exhibited outstanding biodegradability. Therefore, the copolymer, derived from castor oil and behenyl acrylate, holds promise as a potential environmentally friendly multifunctional additive for lubricating oil.

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