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Evaluation and Synthesis of Environmentally Benign Multifunctional Additives for Lube Oil

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

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

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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) [4], pour point depressants (PPD) [5], detergent-dispersants [6] and antiwear agents [7].

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. MATERIALS 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.

2.2 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 following the method as reported elsewhere [16]. 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 room temperature.

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.

3. RESULTS AND DISCUSSION

3.1 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 P-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 1714 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 unsatura-tionfrom-citralportion 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.

3.2 Performance of the Prepared Additives in the Form of Pour Point Depressant

The results of pour point depressant (PPD) properties of the prepared samples, covering a range of additive concentrations within 1 wt% to 5 wt%, are outlined in Fig. 1. The figure vividly demonstrates the efficacy of the prepared addit-ives 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 significant pour point depressant properties.

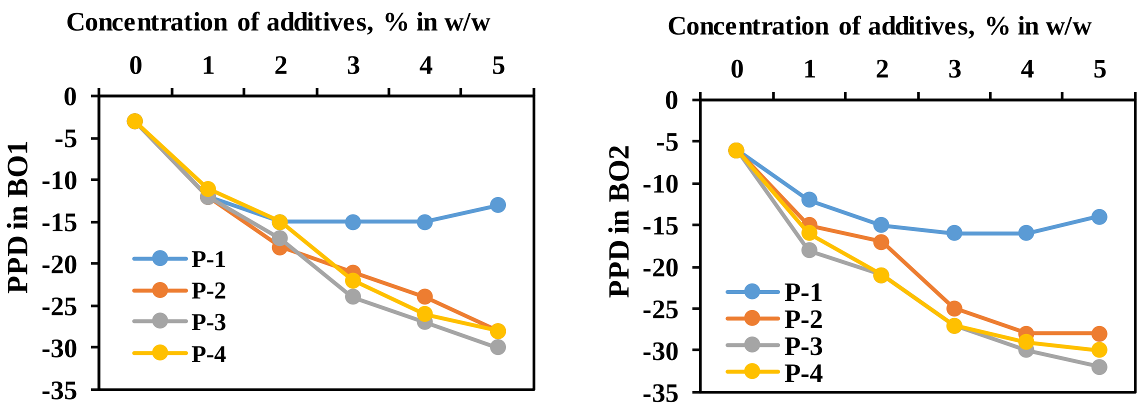

Fig. 1. Pour Point of all the additive doped base oils (BO1and BO2) at a different additive concentration

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].

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

Fig. 3. 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.

3.4 Performance of the Prepared Additives as Anti Wear Additive

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 (Table 1). The most distinct drop was observed at 20 kg load condition, as illustrated in Figs 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.

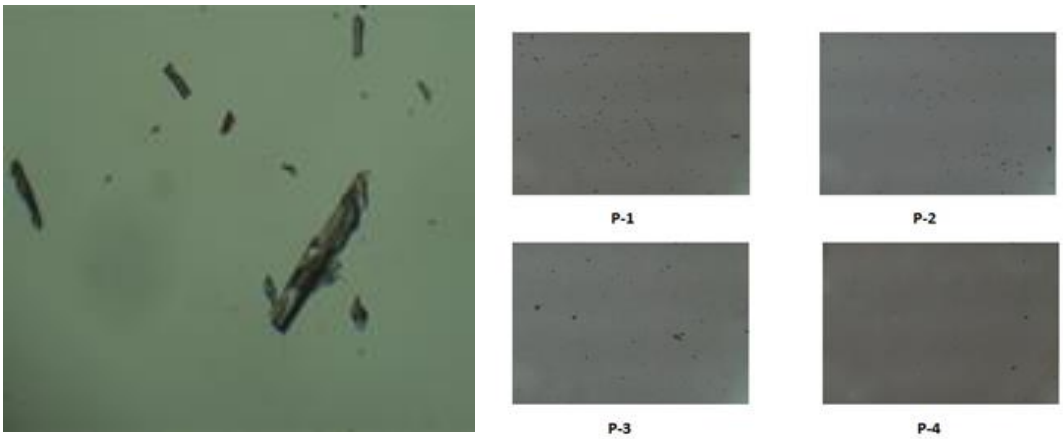

Fig. 2. Photomicrographic images of base oil (left side) and additive (P-1, P-2, P-3 and P-4) Doped base oil (right side)

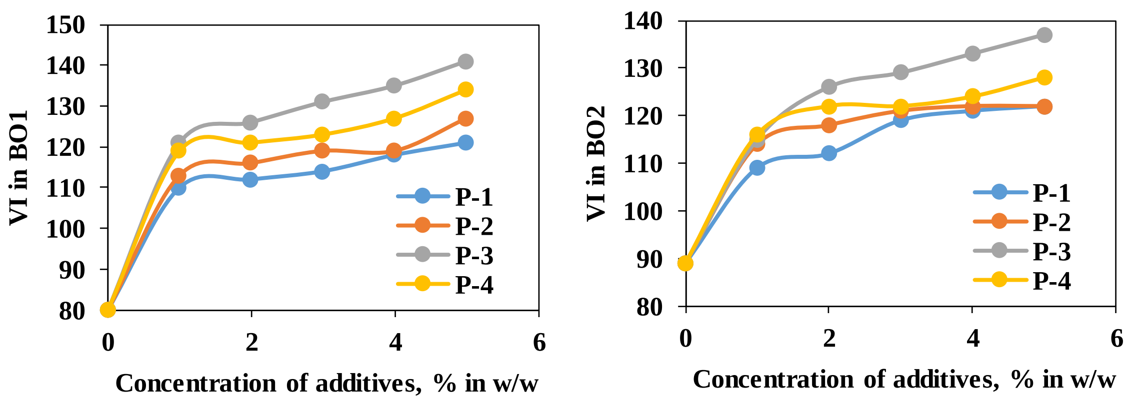

Fig. 3. The VIs corresponding to additive-doped base oils

Table 1. Anti wear values in terms of WSD in mm of polymers P-1, P-2, P-3 and P-4 in the base oils (BO1 and BO2) at 40 kg load

WSD in mm. in BO1 Concentration of the additives, % in w/w							WSD in mm. in BO2 Concentration of the additives, % in w/w					
Sample	0	1	2	3	4	5	0	1	2	3	4	5
P-1	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-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

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 antiwear performance.

3.5 Analysis of Biodegradability Test Result

The biodegradability test results obtained from disc diffusion method and soil burial test (Table 2) indicates notable biodegradability for fungal pathogen Alternaria alternata, compared to the homopolymers. This observation was subst-antiated by the shift in the IR frequency of the ester carbonyl. As anticipated, the copolymer exhibited superior biodegradability in comparison to the homopolymer.

Table 2. 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

3.6 Determination of Molecular Weight of the Polymers

The molecular weight data obtained from the GPC analysis method (Fig. 4) indicates the drop in molecular weight, both Mw and Mn compared to the homopolymers. The GPC data also suggested that the gradual increase in citral concentration in the feed of polymerization resulted in a gradual decrease in the Mol wt and the drop is directly related to the increase in performance of the additive doped base oil upto a certain limit. The poly dispersity index values indicated the linear nature of the polymer chain which is a very significant parameter to yield the best performance of the polymeric additives.

3.7 TGA Data of all the Polymer Samples

Table-3 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.

Table 3. 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

Polymer Samples	Decomposition Temperature (K)	Residual Weight (%)
	605	23
	627	8
P-4	566	85
	589	80
	617	7
	640	5

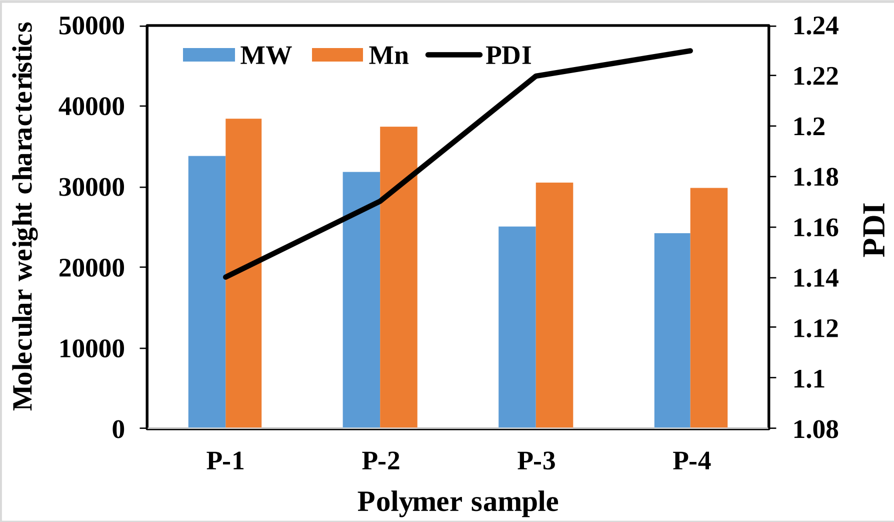

Fig. 4. Molecular weight characteristics of the polymers

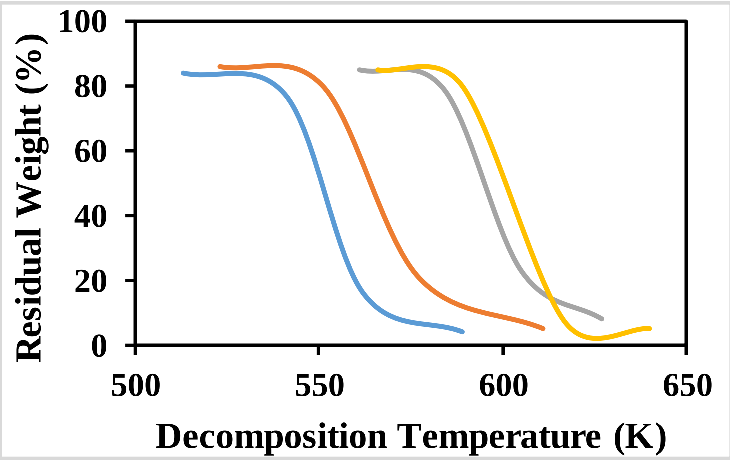

Fig. 5. TGA data for homo and copolymer of behenylacrylate

3.8 Physical Properties of Base Oils

Table 4. 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

4. CONCLUSIONS

All the copolymers (P-2, P-3, and P-4) along with the homopolymer (P-1) demonstrated excellent viscosity index improver (VII), pour point depressant (PPD) and antiwear (AW) properties. Additionally, the copolymer also exhibited significant 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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