



Synthesis of Neem oil - based greener additives for lubricating oil

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Abstract: The depletion of global crude oil reservoir, rising prices of crude oil, and growing environmental concerns represent pressing issues that have the potential to significantly impact human lives. Addressing these challenges requires focused attention from researchers to identify an alternative solution and promote the development of a sustainable environment. This study aims to address these concerns by synthesizing homopolymer Neem oil (NO) and copolymers with N-butyl acrylate without the use of any solvents. Benzoyl peroxide (BZP) is employed as an initiator for polymerization, and the resulting polymers are evaluated as additives for lubricating oils. The synthesized polymers were characterized using the spectral techniques such as FT-IR and NMR spectroscopy. The thermal stability is assessed through thermo-gravimetric analysis (TGA), and the molecular weight is determined using gel permeation chromatography (GPC). The additives' performance as viscosity index improver (VII) and pour point depressants (PPD) is investigated in SN150 mineral oil by standard ASTM method. The biodegradability of all polymers was assessed using the disk diffusion method. The experimental findings and data analysis indicates that the copolymer exhibits promising properties as a multifunctional lubricating oil additive compared to the homopolymer. Additionally, an increase in the concentration of N-butyl acrylate in the copolymer results in higher average molecular weight, improved thermal stability, and enhanced performance as a VI and PPD. This suggests that adjusting the composition of the copolymer can positively enhance its molecular characteristics as well as performance as a lubricating oil additive.

Keywords: Neem oil, Free radical polymerization, Pour point depressant, Viscosity index improver, Biodegradability.

Introduction

Since ancient times, dating back to the invention of the wheel, our ancestors employed both edible and non-edible vegetable oils along with animal fats for lubrication purposes. As mankind progressed and devised mechanical creations, the instinctive use of lubrication became ingrained. A lubricant is a substance that diminishes friction between interacting surfaces, thereby minimizing the heat produced during their movement. Consequently, it serves to shield closely situated surfaces, functioning as an anti-friction medium [1]. An effective lubricant can maintain separation between moving surfaces, exhibit outstanding thermal characteristics, function as a corrosion inhibitor and friction

reducer, repel water, demonstrate exceptional wear resistance, tolerate wear debris, and handle various contaminants [2].

A petroleum-based lubricant consists of a blend of hydrocarbons, including paraffinic (linear/branched), olefinic, naphthenic, and aromatic compounds, each containing 20 to 50 carbon atoms [3]. The makeup of the substance has been identified as both not capable of natural decomposition and not replenish, creating an environmental hazard because of its harmful properties and posing a risk to the survival of living organisms [4]. The excessive use of petroleum-based lubricants has raised environmental concerns, prompting researchers and scientists to seek alternative, biodegradable, and eco-friendly options. Vegetable-based lubricants emerge as a promising substitute due to their biodegradability, non-toxic nature, renew-ability, and lower energy consumption in production, with no waste generation. However, these vegetable-based oils face challenges such as poor thermal stability, oxidation stability, hydrolytic instability and a low viscosity index. These drawbacks can be addressed through chemical modifications or blending with appropriate additives [5]. The incorporation of additives which is polymeric in nature is essential in automotive engine lubrication to improve performance, longevity, and overall efficiency in modern engines. It typically enhances the thermal and oxidative stability, viscosity index, pour point, and anti-wear capabilities of lubricating oil. Additives commonly found in the market are synthetic and petroleum-based, but they are non-biodegradable and pose slight toxicity risks to the environment [6]. Hence, the production of bio additives is a developing field of study within the lubrication sector, characterized by its environmentally friendly nature, biodegradability, and natural availability. Additionally, these additives exhibit favourable attributes such as effective anti-wear properties, a high viscosity index, low volatility, robust thermal stability, pour point depressant and the ability to improve the performance of extreme pressure additives [4].

Neem oil, derived from *Azadirachta Indica*, is rich in triacylglycerols composed mainly of oleic acid ($C_{18}H_{34}O$). The chemical name for oleic acid is Cis-9-octadecenoic acid, characterized by a carbon 18 fatty acid structure with a double bond at C-9. The predominant fatty acid in neem oil is oleic acid (60.402%), which is a polyunsaturated fatty acid. Additionally, it contains notable amounts of saturated fatty acids, including palmitic acid (18.1%) and stearic acid (18.1%). Other fatty acids present in neem oil include linoleic acid (18.3%), linolenic acid (0.2%), arachidic acid (0.8%), caprylic acid (15.933%), and myristic acid [7, 8]. Neem oil finds widespread application in various sectors, including pharmaceuticals, lubricants, nutritional products, agriculture, animal husbandry, cosmetics, and numerous other fields [9,10]. With its elevated molecular weight, viscosity, density, and flash point, it possesses characteristics that make it well-suited for crafting additives in the production of lubricating oil, as well as serving as a component in the formulation of bio lubricants [11, 12]. However, there is limited research available on the utilization of Neem oil-N-butyl acrylate copolymer as a green multifunctional additive for lubricants.

In this study, we conducted the synthesis of a homopolymer derived from Neem oil and copolymers with varying ratios of N-butyl acrylate. The objective was to produce lubricant additives that are thermally stable, economically viable, and environmentally friendly. The selection of N-butyl acrylate was based on its ability to improve the thermal stability of the lubricant. To assess the performance of the synthesized polymeric additives, viscosity index improver and pour point depressants, following the relevant ASTM methods were evaluated.

Experimental section

Materials

Neem oil with a 63% unsaturation level was commercially obtained. Benzoyl peroxide (98%, LOBA Chemie, India) was employed following recrystallization from a chloroform-methanol mixture. N-butyl acrylate was procured from

Sisco Research Laboratories Pvt. Ltd. The mineral base oil SN150 was acquired from Indian Oil Corporation Limited (IOCL), Dhakuria, West Bengal, India. The fungal specimens were collected from Department of Microbiology, North Bengal University, West Bengal, India.

Synthesis of homopolymers and copolymers

The synthesis of copolymers involved the utilization of Neem oil and N-butyl acrylate monomers at varying percentage ratios. This process was conducted through free radical polymerization, employing BZP as the initiator, and was carried out without the use of a solvent. The reaction took place within a three-necked round bottom flask equipped with a magnetic stirrer, thermometer, condenser and an inlet for the introduction of nitrogen. A specific quantity of Neem oil and N-butyl acrylate was subjected to heating at 90° C for duration of 30 minutes. Subsequently, an initiator, BZP, was introduced at a concentration of 0.5% (w/w) relative to the total monomer, and the mixture was heated consistently for 6 hours. Following the completion of the reaction period, the polymerization process was halted by transferring the reaction mixture into cold methanol under stirring. The resultant polymer precipitation was obtained and subjected to further purification by dissolution in a hexane solution, followed by the addition of cold methanol. Finally, the polymer underwent a vacuum drying process at a temperature of 50° C. Similarly, the synthesis and purification of Neem oil homopolymer followed identical procedures [13].

Spectroscopic measurement

Nuclear Magnetic Resonance (NMR) spectra were acquired using a BRUKER AVANCE II 400 FT-NMR spectrometer equipped with a 5 mm BBO probe. The solvent employed was dimethyl sulfoxide (DMSO) and tetramethylsilane (TMS) served as the reference substance. Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8300 spectrometer with 0.1 mm KBr cells at room temperature, spanning the wave number range from 400 to 4000 cm⁻¹.

Molecular weight determination by GPC

The GPC apparatus, featuring UV/Visible detector (2489), refractive index detector (2414), and HPLC Pump (515), was employed to assess both the number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer. Tetrahydrofuran (THF) was used as the solvent in these analyses.

Thermo Gravimetric Analysis (TGA)

The evaluation of the polymer's thermal stability was conducted using Shimadzu TGA-50 systems, with a heating rate set at 10° C per minute in air using an alumina crucible.

Performance evaluations

Evaluation of viscosity index (VI)

Viscosity index which is one of the important parameters in the determination of the resistance of the change of viscosity of the lubricant with the increase in temperature was calculated according to ASTM-D 2270-10 method. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40° C and 100° C. Additives of different concentrations were blended with the lube oil to evaluate the effect of concentration of additives in VI.

Evaluation of pour point

The pour point analysis of the additive doped with lube oil was conducted following the ASTM-D 97-09 procedure using the WIL-471 cloud and pour point tester, manufactured in India.

Biodegradability Test

The environmental destiny of a substance is primarily determined by its biodegradability, with a crucial distinction observed between vegetable-based oils and mineral oils. Unlike mineral oils, vegetable-based oils readily undergo biodegradation, particularly in anaerobic conditions [14]. Ultimate biodegradation denotes the complete transformation of a substance by microorganisms into carbon dioxide, water, mineral salts, and biotic mass. Various tests have been devised to assess biodegradability with the disc diffusion method employed in this study to evaluate the microbial degradation of polymers against fungal pathogens.

Disc Diffusion Method.

In this process, biodegradation of the prepared polymer samples were tested against fungal pathogens namely *Alternaria alternata*. All glass apparatus, culture media were autoclaved before use. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. The fungal growth was confirmed by a change of colour from yellow to blackish. The experiment was performed in Petri dishes and was incubated at 37°C for 30 days after addition of definite weight of polymer samples. The whole process was carried out in inoculation chamber. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed [15,16].

Results and discussions

Spectroscopic data analysis

The homopolymer exhibited an infrared absorption peak at 1741.44 cm^{-1} , while the copolymer displayed a peak at 1737.65 cm^{-1} , indicating the presence of ester carbonyl groups. Similar findings were reported in the infrared spectra of other polymers.¹⁴ The homopolymer showed peaks at 1163.45 cm^{-1} and 1114.38 cm^{-1} , corresponding to the ester C-O stretching vibration of ester carbonyls. Similarly, the copolymer exhibited peaks at 1164.8 cm^{-1} and 1164.18 cm^{-1} for the same vibration, consistent with previously reported results.¹⁵ Peaks at 712.33 cm^{-1} for the homopolymer and 735.84 cm^{-1} for the copolymer indicated C-H bending vibrations. Absorptions in the range of 2923.12 cm^{-1} to 2853.59 cm^{-1} for the homopolymer and 2923.98 cm^{-1} to 2854.47 cm^{-1} for the copolymer were attributed to the stretching vibration of C-H bonds in $-\text{CH}_2-$ groups. There is no notable peak observed in the range of olefinic bonds ($1640 - 1680\text{ cm}^{-1}$) that could serve as an indication of polymer formation. (Figure 1 and Figure 2)

The ^1H NMR spectra of both Neem oil homopolymer and its copolymer with N-butyl acrylate reveal peaks within the 2.5 ppm to 2.7 ppm range, which signify the presence of protons associated with the $-\text{OCH}_2$ groups of Neem oil and N-butyl acrylate. Additionally, peaks observed between 0.6 ppm to 1.5 ppm indicates the presence of methyl protons and 1.8 ppm to 2.5 ppm suggest the existence of methylene protons of Neem oil and N-butyl acrylate. In the copolymer, the appearance of peaks between 3.5 ppm to 4.5 ppm indicates the presence of protons from $-\text{COOCH}_2$ groups. The formation of homopolymer was suggested by the absence of peaks in the unsaturation region between 3.5 ppm and 5.0 ppm. The creation of a copolymer of Neem oil and N-butyl acrylate was confirmed by the absence of peaks within the 5.5 ppm to 6.5 ppm range, indicating the successful completion of the polymerization process.

In the ^{13}C NMR spectra of both the homopolymer and copolymer derived from Neem oil, the ester carbonyl group is observed within the range of 167 ppm to 176 ppm. Additionally, the carbon of $-\text{OOCH}_2$ group of Neem oil are detected

between 61 ppm and 70 ppm. The absence of peak at 73 ppm suggests the non-existence of –OH groups in the Neem oil homopolymer. Moreover, the absence of peaks in the range of 135 ppm to 165 ppm indicates the successful completion of polymerization.

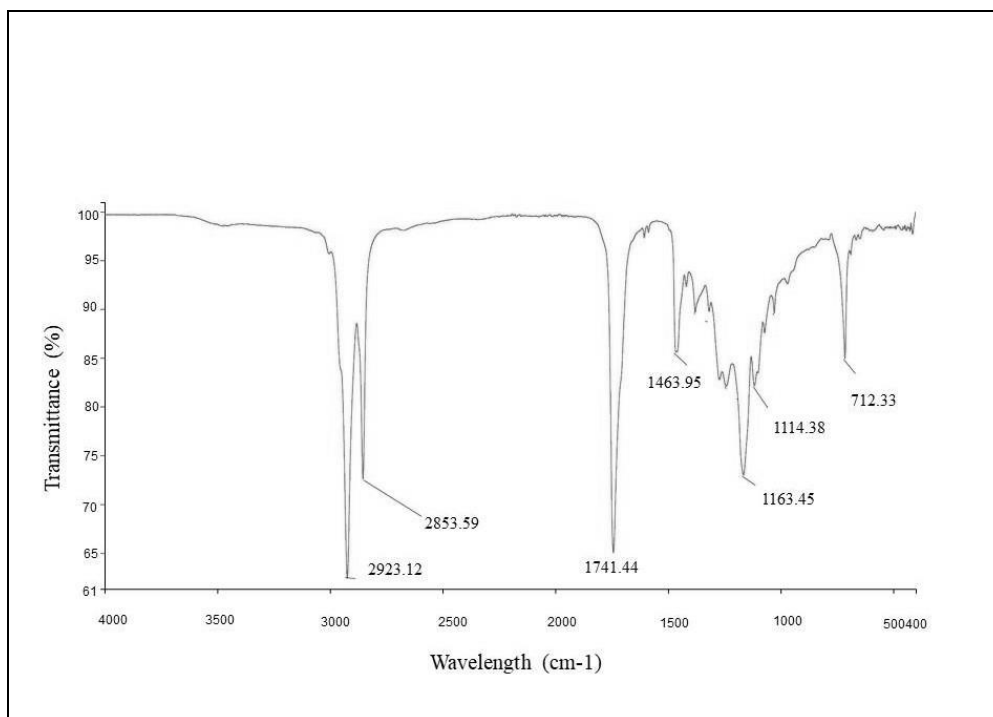


Figure 1: FT-IR of Homopolymer of Neem oil (P-1)

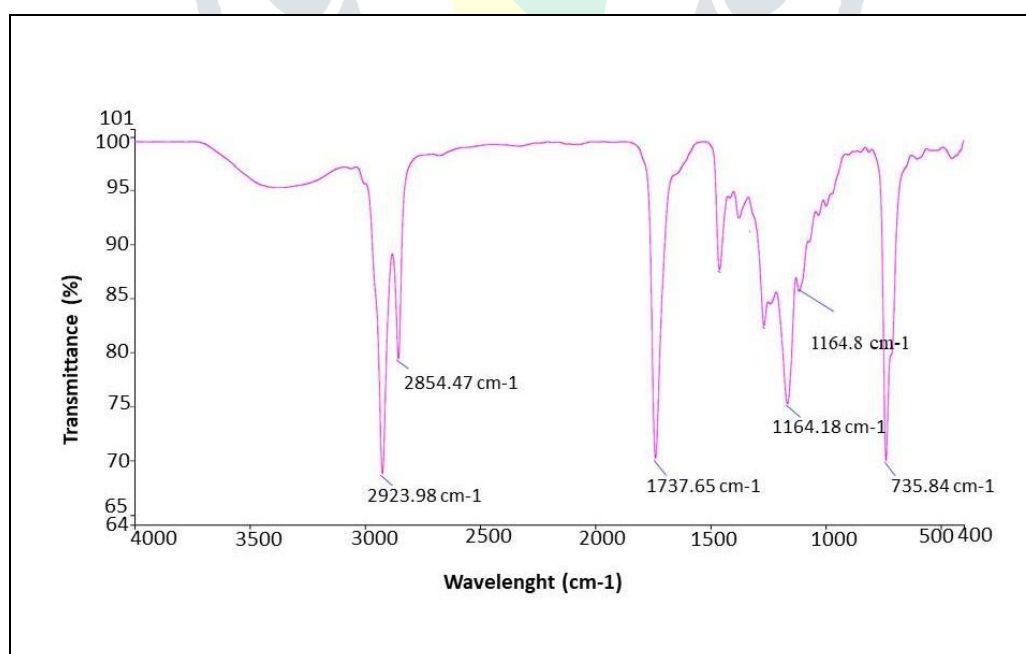


Figure 2: FT-IR of Comopolymer of Neem oil (P-2)

Molecular weight data analysis

The weight average (M_w) and number average (M_n) molecular weights of the synthesized polymers (P-1 to P-5) was determined by using Gel Permeation Chromatography at room temperature in THF shown in Table 1. Analysis of the experimental results, reveals that P-5 exhibits the highest molecular weight among the five polymers. Additionally, there is a clear correlation between the molecular weight and the percentage of N-butyl Acrylate in the Neem oil backbone; as the percentage of N-butyl Acrylate increases, the molecular weight also increases[17]. This highlights the significant influence of N-butyl Acrylate on the polymerization reaction.

Table 1: M_n , M_w and PDI values of the prepared polymers

Polymer Code	M_n	M_w	PDI
P-1	8413	8580	1.0198
P-2	8674	8802	1.0147
P-3	8756	8965	1.0238
P-4	8890	11041	1.2419
P-5	10,798	11,786	1.0914

P-1 – 100% of NO, P-2 – 97.5% of NO + 2.5% N-butyl Acrylate, P-3 – 95% of NO + 5% N-butyl Acrylate, P-4 – 92.5% of NO + 7.5% of N-butyl Acrylate, P-5 – 90% of NO + 10% N-butyl Acrylate. NO – Neem oil, M_n – Number average molecular weight, M_w – Weight average molecular weight, PDI – Polydispersity index.

Thermo gravimetric analysis

The TGA values of the five prepared polymers are shown in Figure. 3. It is evident from the figure that the homopolymer P-1 is found to be thermally less stable because the thermal degradation of P-1 is higher than the other copolymers P-2, P-3, P-4 and P-5. The thermal degradation of polymer P-2, P-3, P-4 and P-5 are seen to be almost similar. With the increase in the concentration of Neem oil in the feed, there is an increased in thermal stability. The major decomposition of homopolymer P-1 and copolymer P-2 start at 250° C with a 25% weight loss and 300° C respectively. Thermal stability of the prepared polymer increases due to the copolymerization of Neem oil with N-butyl Acrylate. Therefore, copolymerisation with N-butyl Acrylate is an important parameter to enhance the thermal stability of the polymer which is considered as essential criteria for the additive for lube oil.

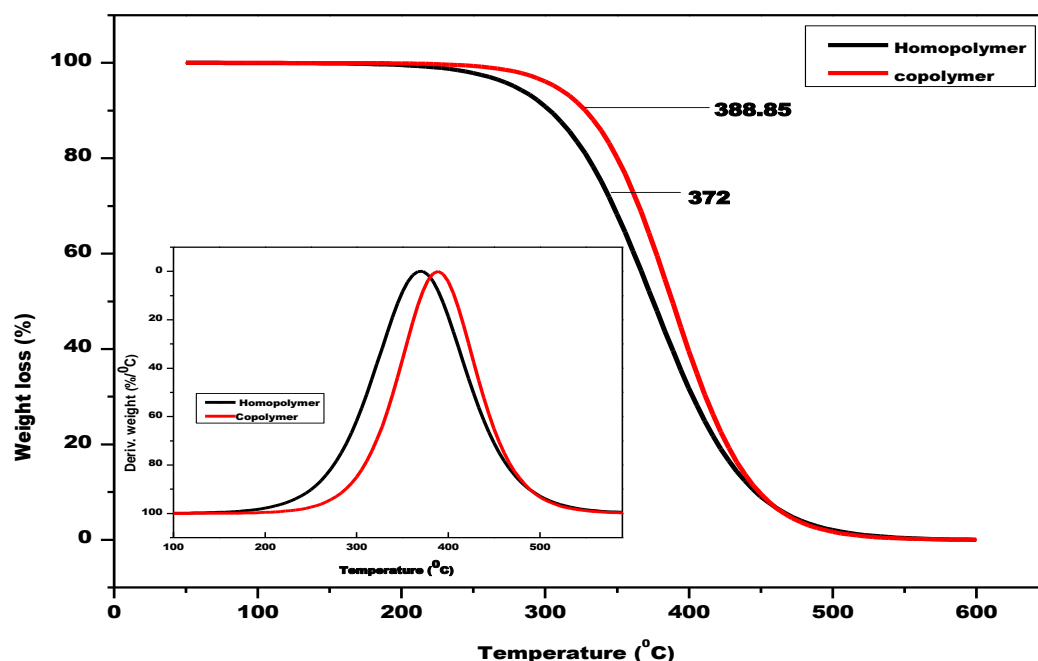


Figure 3: TGA curve of the prepared polymers P-1 and P-2

Analysis of Viscosity index (VI) value

The experimental VI values obtained for various concentrations (ranging from 1% to 5% w/w) of polymeric additive samples mixed with base oil are shown in Table 2. The analysis reveals that the viscosity index (VI) rises with the escalating polymer concentrations in the base oil. Among the copolymers, P-5 exhibits the most significant impact on VI, followed by P-4, P-3, P-2, and P-1. This demonstrates that copolymers function more effectively as viscosity modifiers compared to homo polymers. The incorporation of N-butyl acrylate into the Neem oil homo polymer backbone leads to an increased VI, likely attributed to the higher cross-link density of the resulting copolymers [18,19]. The superior VI of copolymer P-5 can also be attributed to a larger volume of solvated additive molecules (micelles) due to its higher average molecular weight and lower polydispersity index (PDI). Elevated temperatures typically reduce the viscosity of lubricating oil, but the increased concentration of polymer in the base oil at higher temperatures enlarges the volume and size of polymer micelles [20]. This counteracts the viscosity decrease of the base oil. Additionally, higher polymer concentrations enhance the viscosity index property, contributing to improved performance.

Analysis of pour point values

The polymer additives, synthesized for use as pour point depressants (PPDs) in base oil, were evaluated. Pour points of lubricants blended with polymers at concentrations ranging from 1% to 5% (w/w) were experimentally determined and shown in Table 2. The results revealed that copolymers P-2 to P-5 exhibited superior PPD performance compared to homopolymer P-1, with P-4 proving to be the most effective. The efficiency of these prepared polymers in reducing pour points was notable, showing an increase in effectiveness with polymer concentrations up to 4%. This suggests that at this concentration, the polymer interacts with the paraffinic wax in the base oil more effectively, leading to a reduction in the size of paraffinic wax crystals [21, 22]. Particularly, P-4 polymer demonstrated enhanced pour point depressant performance, likely attributed to its higher polydispersity index (PDI) value [23].

Table 2: Viscosity index(VI) and pour point (PP) values of lubricants at different concentrations (w/w)

Poly. code	VI/ PP	0%	1%	2%	3%	4%	5%
P-1	VI	84.6	96	100	112	120	134
	PP	-5	-8	-8	-11	-14	-14
P-2	VI	84.6	102	117	123	143	145
	PP	-5	-7	-7	-11	-16	-15
P-3	VI	84.6	117	146	154	160	166
	PP	-5	-8	-10	-11	-16	-16
P-4	VI	84.6	135	189	178	182	199
	PP	-5	-8	-10	-14	-20	-20
P-5	VI	84.6	185	199	200	220	267
	PP	-5	-8	-11	-13	-18	-15

Biodegradability test

The examination for biodegradability involved subjecting the polymers to a disc diffusion method against the fungal pathogen *Alternaria Alternata* and is shown in Figure. 4 which provides the loss percentage of mass following polymer biodegradation. The outcome of the biodegradability assessments revealed that, among the five polymers assessed, P-1 exhibits high biodegradability, while P-5 demonstrates the lowest. Consequently, the use of Neem oil is notably important in promoting the biodegradability of these additives.

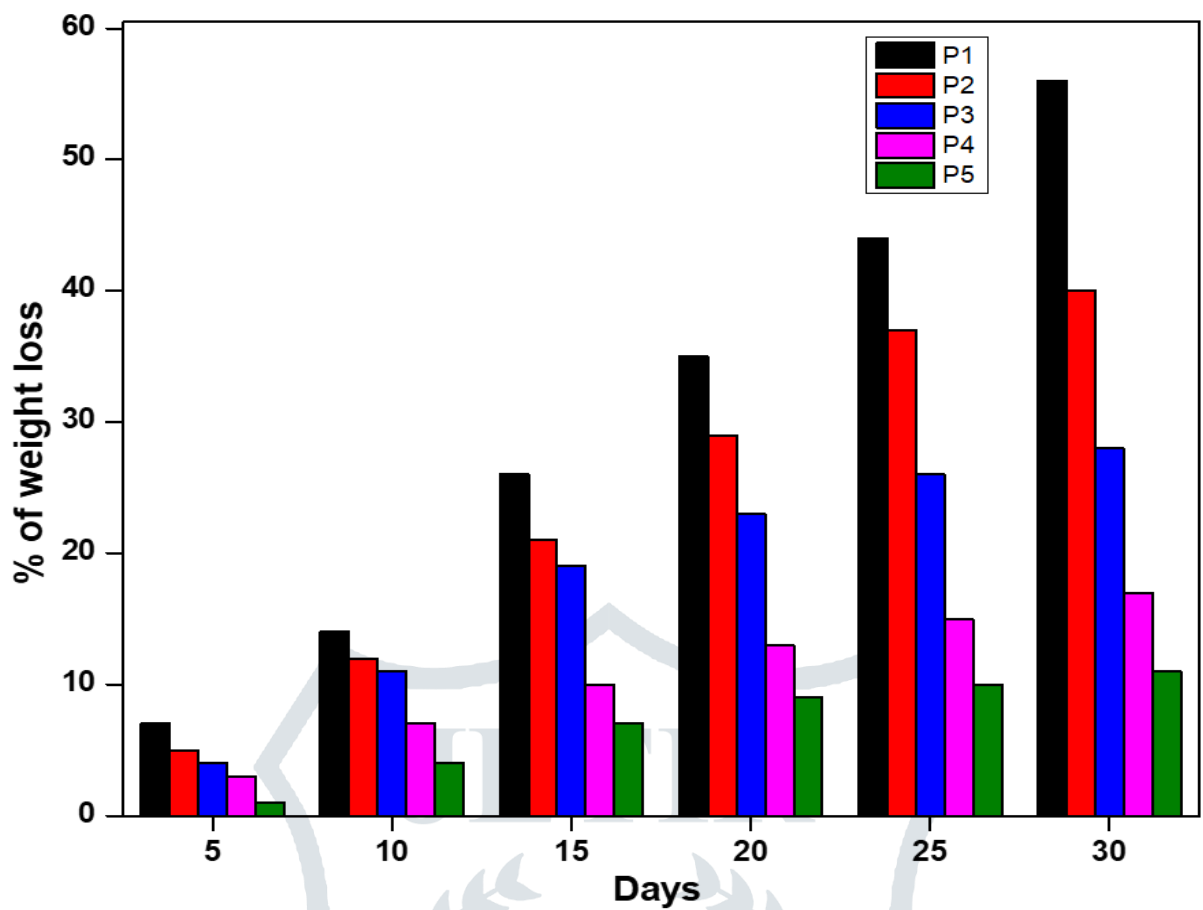


Figure 4: Biodegradability test of the lubricant compositions

Conclusions

The research findings indicated that both the homopolymer of Neem oil and its copolymer with N-butyl acrylate exhibit enhanced performance as viscosity index (VI) improvers and pour point depressants (PPD) for base oil. Copolymers were found to be more effective than homopolymers in these applications. The average molecular weight, thermal stability, and viscosity index (VI) improver’s enhancement properties of the copolymers improved as the proportion of N-butyl acrylate in the copolymers increases. The efficacy of the additives as pour point depressants (PPD) rises with additive concentration, peaking upto 4% concentration. It is also obtained that the homopolymer demonstrates greater biodegradability compared to copolymers, and the biodegradability diminishes with an increase in the N-butyl acrylate content in copolymers. Consequently, this study represents a promising approach to developing an environmentally friendly lubricant composition.

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