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Synthesis of Copolymer from Industrial Waste as Modifier for Iraqi Lubricants

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General Background: The increasing global demand for sustainable practices in the lubricants industry has highlighted the potential for utilizing industrial waste to enhance lubrication formulations. Specifically, the use of polyethylene wax derived from industrial waste offers a promising avenue for improving polymer performance. **Specific Background:** In Iraq, the development of lubricating oil formulations utilizing locally sourced industrial waste remains underexplored. The synthesis of copolymers from polyethylene wax and alkyl acrylates presents a novel approach to improving the efficiency of lubricants. **Knowledge Gap:** While numerous studies have focused on the role of polymer additives in lubrication, there is a lack of research on the application of waste-derived copolymers, particularly in the context of the Iraqi oil industry. **Aim:** This study investigates the synthesis and characterization of poly(2-ethylhexyl acrylate-co-polyethylene wax) (TND-W) copolymer derived from industrial waste, and evaluates its efficacy as a viscosity modifier (VM) and pour point depressant (PPD) in lubricating oils. **Results:** The synthesized copolymer demonstrated significant improvements in the viscosity and pour point properties of base oils. The copolymer's performance was shown to be concentration-dependent, with the optimal performance observed at 4000 ppm. However, increasing the concentration beyond this level resulted in reduced effectiveness due to solubility limitations in the base oils, especially at lower temperatures. **Novelty:** This research introduces a sustainable approach to enhancing lubricating formulations by utilizing industrial waste materials, a method not commonly explored in previous studies within the context of the Iraqi oil industry. **Implications:** The findings provide valuable insights for the oil industry, particularly in the development of eco-friendly lubricants. The study's implications extend to environmental sustainability, suggesting a practical solution for incorporating waste-derived materials into industrial applications.

Highlights:

- Synthesis of a copolymer from industrial waste for use in lubricating oils.
- Demonstrated the copolymer's dual functionality as a viscosity modifier and pour point depressant.
- Highlighted the concentration-dependent effectiveness of the copolymer, with optimal performance at 4000 ppm.
- Offered a sustainable approach to improving oil formulations, contributing to both environmental and performance enhancement.

Keywords: Copolymer, Lubricating Oil, Polyethylene Wax, Pour Point Depressant, Viscosity Modifier (VM)

Introduction

Lubricating oils comprise a diverse array of chemicals recognized for their essential function in minimizing friction and facilitating the effective operation of machinery and engines. These oils comprise diverse constituents predominantly sourced from the residual, very viscous portion of crude oil following the distillation process [1] [2]. To meet the stringent requirements of original equipment manufacturers, contemporary lubricants undergo precise engineering that involves the integration of essential liquids and chemical additives [3] [4] [5] [6] [7]. The majority of commercially available lubricants are compounded oils, comprising base stocks and additives that enhance performance. When these components are present in their required quantities, they impart the necessary qualities for optimal performance in the intended application. In addition to their fundamental tasks of lubrication, cooling, containment, and suspension, as well as corrosion protection and power transmission, these lubricants must also perform specific duties unique to each application [3]. Various additives can be employed in multiple applications to enhance the efficacy of lubricants. These additives include corrosion inhibitors, viscosity modifiers (VM), antioxidants, pour point depressants (PPD), dispersants, and detergents [7] [8] [9] [10] [11]. The viscosity of the lubricant is a critical component to consider when selecting a lubricant. If the viscosity of the lubricant oil is excessively low at the operational temperature, the lubricant film fails to form adequately, leading to wear, overheating, and adhesion. If the viscosity is elevated, its resistance increases, leading to heightened thermal friction and thus, atypical power loss [6]. Consequently, VM and PPD are significant additions to lubricating oil. This research concentrates on VM. Oil with increased viscosity is more viscous than oil with reduced viscosity. At elevated temperatures, oil exhibits reduced viscosity and flows more readily; conversely, at lower temperatures, it becomes more viscous. [6] [12] The variation in dynamic viscosity resulting from temperature changes is measured using the BROOKFIELD Viscometer, model RVDV-II+ P (USA), with a torque range of Decal. The spindle type (18) is utilised to assess viscosity, shear rate, and shear stress. A higher VM number indicates that the viscosity of the lubricant oil remains relatively consistent across different temperature fluctuations [1]. Diverse polymeric substances have been suggested as prospective additions for lubricating lubricants [3] [4] [13] [14]. Viscosity modifiers (VMs) are characterized by their elongated hydrocarbon side chains and elevated molecular weights [15] [16] [17] [18]. The efficacy of these additives depends on their capacity to enhance an oil's relative viscosity at elevated temperatures rather than at lower temperatures. This conclusion typically results from a change in the polymer's physical configuration when the mixture's temperature rises. The polymer molecule in the solution exists as a disorderly coil, which is expanded by the lubricant oil solvent.[19] The solubility of polymers generally increases with temperature, as the polymer molecules transition from compact coils to a more extended configuration, leading to a greater overall volume. The increased volume elevates the viscosity of lubricating oil, counteracting the typical reduction in viscosity associated with rising temperatures [20] [21]. The volume of polymer in an oil solution escalates with an increase in the polymer's molecular weight [22]. Consequently, in comparison to a lower molecular weight polymer of the same kind, a higher molecular weight polymer will confer a greater viscosity modulus [2].

Polymethacrylate was the initial viscosity enhancer researched and developed. The initial research was performed under the guidance of Herman Bruson, who was affiliated with the Rohm and Haas Company [23]. Subsequently, other researchers have enhanced the efficacy of these compounds using various methodologies [9] [24] [25]. This study examines the utilisation of polythene wax, an industrial byproduct, to improve the efficacy of polymethacrylate viscosity enhancers. Polythene wax, characterised by its elevated molecular weight and elongated hydrocarbon chains, provides an economical method to enhance the key components of polyacrylates in contemporary lubricants. This study investigates the molar ratio of polyethylene wax and 2-ethylhexyl acrylate to determine the optimal effectiveness of poly(2-ethylhexyl acrylate-co-polyethylene) in conjunction with lubricating oil. Furthermore, we examined the effect of different amounts of this addition on oil performance.

Method

A. Experimental Section

1. Materials

All the chemicals and solvents used were of analytical grade and supplied by Fluka, Merck, and Aldrich. Benzoyl peroxide, carbon tetrachloride, and dimethyl sulfoxide were obtained from Sigma-Aldrich. Toluene, acetone, methanol, tetrahydrofuran, and dimethylformamide were obtained from Fluka. 2-ethylhexyl acrylate is a Merck product. The polyethylene wax was supplied by The General Company for Petrochemical Industries in Basrah/Iraq. Thin-layer chromatography (TLC) was carried out by using an aluminium sheet coated with silica gel $60F_{254}$ (Merck), and iodine and ultraviolet (UV) light were used for visualizing TLC plates. The free additive medium viscosity lube oils (base oils 40 and 60) from the Al-Daura Refinery in Iraq were used in this study. Table 1 shows the physicochemical properties of lubricating oils.

Specification	40 stock	60 stock
Kinematic viscosity at 40 °C,cSt	18.1	66.5
Kinematic viscosity at 100 °C,cS	3.14	8.84
Viscosity Index	110	105
Specific Gravity at 15.6 °C	0.846	0.8857
Pour Point, ºC	-8	-5

Table 1. The physicochemical characteristics of lube oils

2. Instrumentation

The FT-IR spectra as KBr discs were recorded in the range 4000-400 cm^{-1} using the Shimadzu FT-IR model 8400s instrument. The experimental values of the ^{1}H and ^{13}C NMR spectra for the studied compound were obtained using a Bruker spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) with DMSO-d_6 as the solvent and TMS as the internal standard (Central Laboratory, University of Tehran, Iran). The Thermal analysis (TGA) technique was conducted using a TGA Q500 V6.7 (Germany) at a heating rate of 10 °C min-1 for a temperature range of 25 to

800 °C under a nitrogen atmosphere with a flow rate of 25 mL min^{-1}. Gel permeation chromatography (GPC) was used to determine the molecular weights of variously produced polymer. The analysis was conducted at 25 °C with a flow rate of 1 mL min^{-1} and a sample volume of 50 µL on a 300 mm Jordy Gel DVB mixed column. Viscosity was measured by using the instrument (BROOKFIELD Viscometer torque range Decal), model RVDV-II+ P (USA). Spindle type (18) is used to measure viscosity, shear rate, and shear stress.

B. Synthesis Method

1. Synthesis of poly (2-ethylhexyl acrylate-co-polyethylene) (TND-W)

Synthesis of poly(2-ethylhexyl acrylate-co-polyethylene). Free radical polymerisation was employed. A solution comprising 2-ethylhexyl acrylate (0.05 mol), polythene wax (0.05 mol), and 1% w/w benzoyl peroxide was prepared in 25 mL of anhydrous toluene within a 250 mL three-neck round-bottom flask equipped with a condenser, thermometer, and a glass tube for gas inlet. The reaction mixture underwent argon purging for 15 minutes, followed by progressive heating with a magnetic stirrer to the reflux temperature and a moderate argon flow rate. Heated to 95-100 °C and subsequently chilled after 6 hours. The product was purified using anhydrous tetrahydrofuran and methanol, which were dried over 24 hours at room temperature (25 °C) to yield a white, waxy copolymer. The reaction's completion and the product's purity were confirmed by TLC using a methanol-to-carbon tetrachloride ratio of 2:8. The Rf value of poly(2-ethylhexyl acrylate-co-polyethylene) is 0.82, with a yield of 67%. The synthetic methods for the synthesis of copolymer (TND-W) are depicted in Scheme 1.[26]

2. Poly (2-ethylhexyl acrylate-co-polyethylene) (TND-W)

White waxy copolymer; yield: 67 %; R_f: 0.82; IR (KBr) cm^{-1}: 2916 ν(CH_2, Asymmetrical, str.), 2850 ν(CH, Symmetrical, str.), 1732 ν(C=O, ester group), 1465-1411 ν(CH groups, bending), 1230-1172 $\nu_{str.}$(C-O, ester group); ^{1}HNMR (400 MHz, DMSO-d_6) (δ/ppm): 4.095 (d, 2H, J = 8 Hz, CH_2-O), 2.68 (m, 1H, CH-C=O), 2.055 (m, 1H, CH-CH_2-O), 1.985 (qu, 2H, $J_1 = J_2$ = 8 Hz, CH_2-j), 1.895 (qu, 2H, $J_1 = J_2$ = 4 Hz, CH_2-f), 1.825 (m, 6H, CH_2-h, CH_2-k, CH_2-n), 1.75 (m, 2H, CH_2-g), 1.455 (d, 3H, J = 4 Hz, CH_3-a), 1.21 (d, 3H, J = 8 Hz, CH_3-L), 1.05 (t, 3H, $J_1 = J_2$ = 4 Hz, CH_3-i), 0.85 (t,3H, $J_1 = J_2$ = 8 Hz, CH_3-m); ^{13}CNMR (100 MHz, DMSO-d_6) (δ/ppm): 166.98, 68.87, 50.60, 46.88, 35.41, 33.91, 32.30, 27.26, 26.35, 22.54, 17.21, 16.30, 15.73, 13.82.

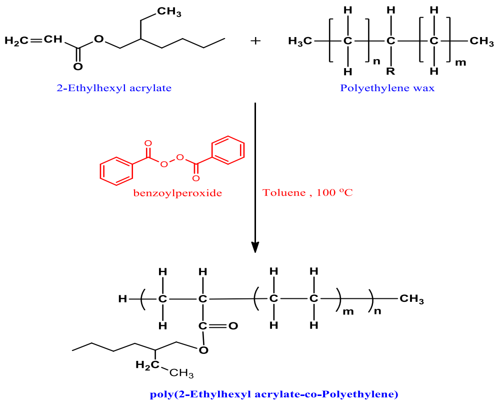


Figure 1. Schematic diagram of free radical copolymerization of 2-ethylhexyl acrylate and polyethylene wax

C. Measurement Methods

1. Evaluation of Prepared Copolymer as Pour Point Depressant (PPDs)

The ASTM D97 standard method was used to evaluate laboratory-prepared copolymers as pour point depressants when mixed with oils at different concentrations (1000-5000 ppm). Initially, samples of oils to which concentrations of the copolymer were heated separately, at a temperature of 70 ºC. With continuous stirring for 40 minutes, the samples are left to cool at laboratory temperature to ensure that the polymer is completely dissolved.

Then, the samples are placed in a large test tube, and a temperature gauge is inserted inside it (a thermometer ranging from 40 to -40 degrees). It is fixed well so that the bulb of the thermometer is positioned inside the model and not touching the bottom of the tube. Then, the tubes are placed in the device, and after the operation, the temperatures gradually decrease. This is evident from the gradual and continuous decrease in the temperature of the samples, as they are checked after every two degrees by removing the tube and moving it each time until the material freezes. Completely, and it stops being fluid, then the degree of spillage is recorded.

The same method mentioned above is repeated to evaluate the performance of all other inhibitors on the lubricating oils and record the results for comparison with the degree of spillage for each oil without adding polymer.[27]

2. Evaluation of Prepared Polymer as a Parameter Improver for Dynamic Viscosity

A Brookfield rheometer [13], as shown in Figure 2, was used to examine the flow characteristics of the base oil sample before and after the addition of the copolymer additive. The base oil sample was prepared by mixing the prepared copolymer (10% by weight) with the free additives oil (base oils 40 and 60) at both temperatures (40°C and 100°C) at different speeds (rpm = 5, 20, 50, and 100).

Figure 2. Rheometer Brookfield viscometer

Results and Discussion

This paper examines the newly synthesized copolymer produced from 2-ethylhexyl acrylate and polyethylene wax, focusing on the conditions pertinent to its production and purification reactions.

The poly(2-ethylhexyl acrylate-co-polyethylene) (TND-W) was synthesized via free radical copolymerization of 2-ethylhexyl acrylate and polyethylene wax, utilizing benzoyl peroxide as the initiator.

This study utilized many approaches to identify and describe the synthesized molecule, including FTIR, ^{1}H NMR, ^{13}C NMR, gel permeation chromatography (GPC), and thermogravimetric analysis (TG/DTG).

1. Spectroscopic Analysis

The spectral studies, including the obtained spectroscopic data for the title chemical, are discussed. The synthesized copolymer exhibited a spectroscopic analysis that aligned with the empirical structure.

2. Infrared Spectrum (FT-IR) of poly(2-Ethylhexyl acrylate-co-Polyethylene)

Infrared spectroscopy is an effective technique employed to characterize this copolymer. The infrared spectrum displays the locations and intensities of the peaks associated with different groups in the copolymer (TND-W).

The absorption bands at 2916 cm^{-1} and 2850 cm^{-1} correspond to the asymmetric and symmetric stretching of the -CH_2 group, respectively, with an observed increase in intensity related to the elongation of the acrylate hydrocarbon chain in the synthesized copolymer. The bands at 1465 and 1411 cm^{-1} are attributed to the bending vibration of the -CH group.[28] A strong peak at 1732 cm^{-1} is attributed to the v(C=O) acrylate group, as illustrated in Figure 2. Simultaneously, two peaks at 1230 and 1172 cm^{-1} correspond to the C–O bond stretching of ester groups.[29] The absence of the vC=C absorption between 1650-1600 cm^{-1}, indicative of a monomer, substantiates the development of the copolymer and confirms that polymerization has occurred.[29]

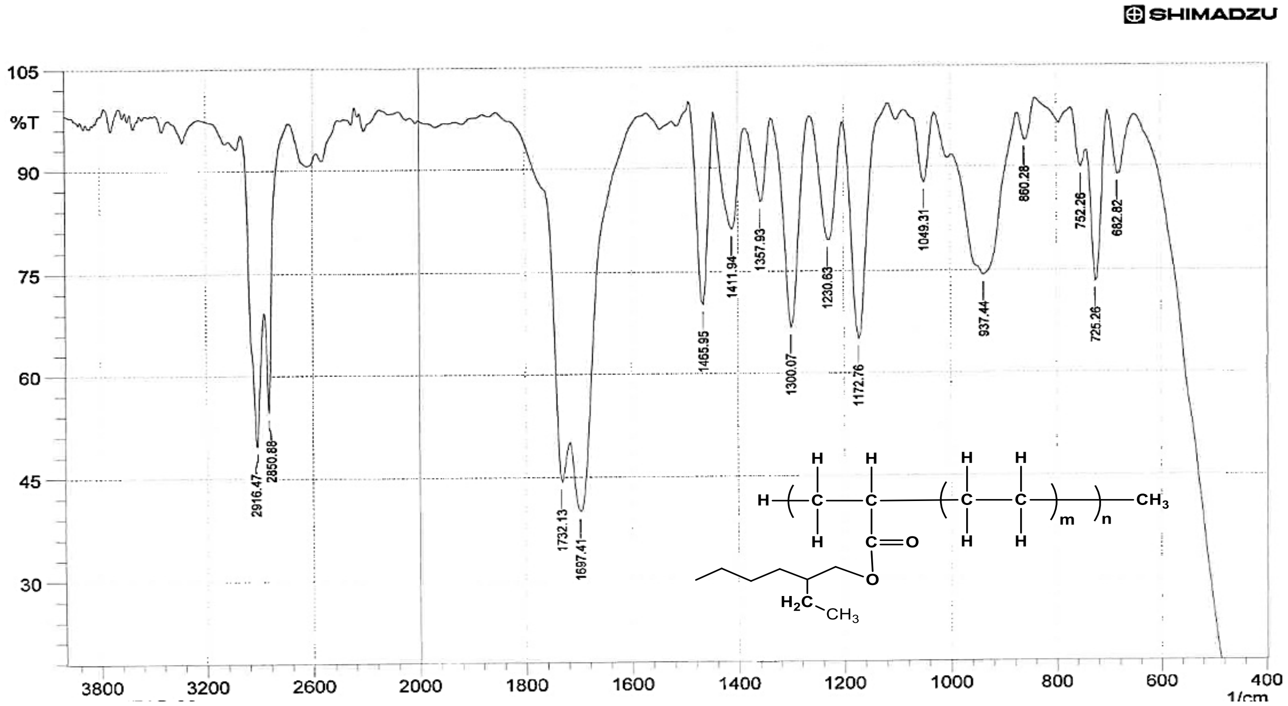


Figure 3. FT-IR spectrum of copolymer (TND-W)

^{1}HNMR and ^{13}CNMR Spectra: The ^{1}HNMR measurement was used to confirm the copolymer (TND-W) structure, as shown in Figure 4 and Table 2. The scientific literature has revealed that ^{1}H-NMR spectroscopy helps determine the nature and structure of copolymers. In this work, the ^{1}H NMR spectrum of the synthesized copolymer (TND-W) was recorded in a deuterated dimethyl sulfoxide solution, using tetramethylsilane (TMS) as an internal standard. Additionally, the ^{1}H NMR spectrum of the compound confirms the compatibility of the proposed structure. Furthermore, the ^{1}H-NMR spectrum of this new copolymer showed a signal at δ 2.5 ppm due to the DMSO solvent and a signal at□ δ 3.4 ppm due to dissolved water in DMSO.[30] The ^{1}HNMR spectrum of the prepared copolymer shows a doublet signal at δ 4.095 ppm, which is attributed to the (CH_2-O) protons.[31] The copolymer (TND-W) is characterized by showing a multiple signal at δ 2.68 ppm, which can be assigned to the (CH-CO_2-) proton. Triplet signals characterize the ^{1}H NMR spectrum of the copolymer δ□□1.05 ppm and δ□□0.85 ppm, which are attributed to the methyl (CH_3) groups. In addition, multiple signals that appear at δ 1.75-2.055 ppm can be attributed to CH_2 of the alkyl chain in the copolymer (TND-W).[16] Therefore, the ^{1}HNMR result supports the formation of the poly(2-Ethylhexyl acrylate-co-Polyethylene) and the completion of free radical copolymerization.

The ^{13}C-NMR spectrum of the copolymer shows a signal at δ□□(166.98) ppm, which is attributed to the carbonyl carbon (C=O) of ester groups.[31] The copolymer (TND-W) is characterized by showing two signals at δ□□(68.87) ppm and δ□□(50.60) ppm, which can be assigned to the ($\underline{C}H_2$-O) and ($\underline{C}H$-CO_2) groups in poly(2-ethylhexyl acrylate-co-polyethylene), respectively.[32]

Additionally, the copolymer (TND-W) exhibits signals in the range□□ (13.82-17.21) ppm, which can be attributed to methyl groups.[33] Furthermore, the signals of aliphatic carbons of the synthesized copolymer are represented at δ (22.54-46.88) ppm.[33] The ^{13}C NMR spectral data of the copolymer (TND-W) are in accord with the suggested structure. The spectrum of the copolymer is shown in Figure 4, and the chemical shifts of the different types of protons are listed in Table 2.

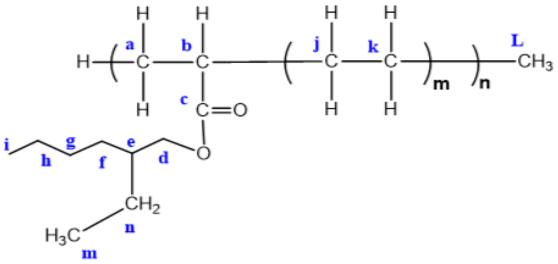
Symbol of com.	Chemical shift of ^{1}H-NMR δ (ppm)	Structural formula
TND-W	0.85 (t,3H, J_1 = J_2 = 8 Hz, CH_3-m) 1.05 (t, 3H, J_1 = J_2 = 4 Hz, CH_3-i) 1.21 (d, 3H, J = 8 Hz, CH_3-L) 1.455 (d, 3H, J = 4 Hz, CH_3-a) 1.75 (m, 2H, CH_2-g) 1.825 (m, 6H, CH_2-h, CH_2-k, CH_2-n) 1.895 (qu, 2H, J_1 = J_2 = 4 Hz, CH_2-f) 1.985 (qu, 2H, J_1 = J_2 = 8 Hz, CH_2-j) 2.055 (m, 1H, CH-e) 2.68 (m, 1H, CH-b) 4.095 (d, 2H, J = 8 Hz, CH_2-d)	
	Chemical shift of ^{13}C-NMR δ (ppm)	
	166.98 (1C, C – c) 68.87 (1C, C – d) 50.60 (1C, C – b) 46.88 (1C, C – e) 35.41 (1C, C – j) 33.91 (1C, C – f) 32.30 (1C, C – g) 27.26 (1C, C – n) 26.35 (1C, C – h) 22.54 (1C, C – k) 17.21 (1C, C – a) 16.30 (1C, C – i) 15.73 (1C, C – L) 13.82 (1C, C – m)	

Table 2. 1H-NMR and 13C-NMR spectrum data of the prepared copolymer (TND-W)

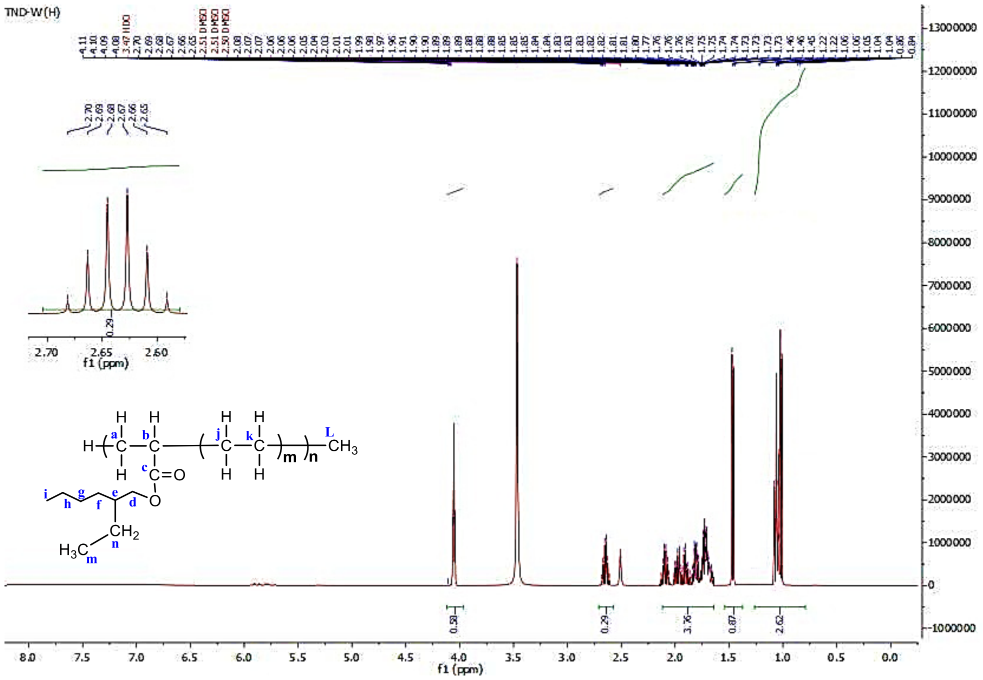


Figure 4. ^{1}H-NMR Spectrum of copolymer (TND-W)

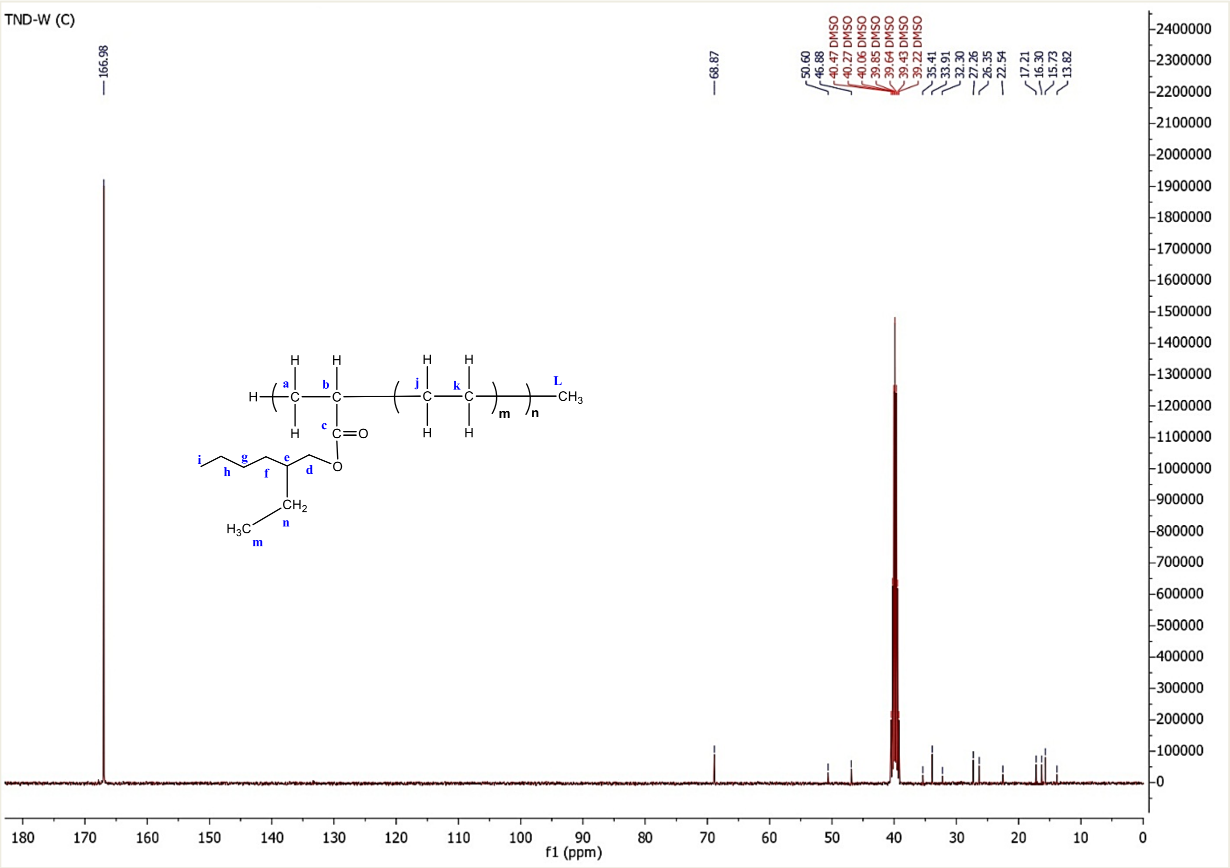


Figure 5. ^{1}C-NMR Spectrum of copolymer (TND-W)

3. Gel Permeation Chromatography (GPC) Measurements

Gel Permeation Chromatography (GPC) is a commonly employed and efficient analytical method in polymer science and other fields. GPC segregates macromolecules according to their size in solution, providing critical information for polymer characterization, molecular weight distribution analysis, and investigation of molecular interactions. A sample is placed into a column containing porous beads (the stationary phase). Bulkier molecules traverse the column more rapidly because they are unable to penetrate the pores, while smaller molecules interact more with the pores, leading to prolonged elution. Detection techniques, including refractive index measurement and light scattering, are utilized to quantify the eluted molecules. GPC is frequently employed to investigate synthetic and biopolymers, proteins, and nanoparticles. GPC is essential in contemporary analytical laboratories by offering comprehensive data on polymer size distribution, molecular weight, and structural alterations [34]. The molecular weight is a crucial characteristic of the produced copolymers, as it aids in evaluating their efficacy as polymer additives for diminishing oil pour point depression (PPD) or improving viscosity. Molecular weights were determined using THF as a solvent for the measurements. The number-average molecular weight (Mn) and the weight-average molecular weight (Mw) were computed [35].

The molecular weight data for the synthesized copolymer are displayed in Table 3 and Figure 6. A discernible tendency is the progressive rise in weight-average molecular weight (Mw) corresponding to the elongation of the side chain.

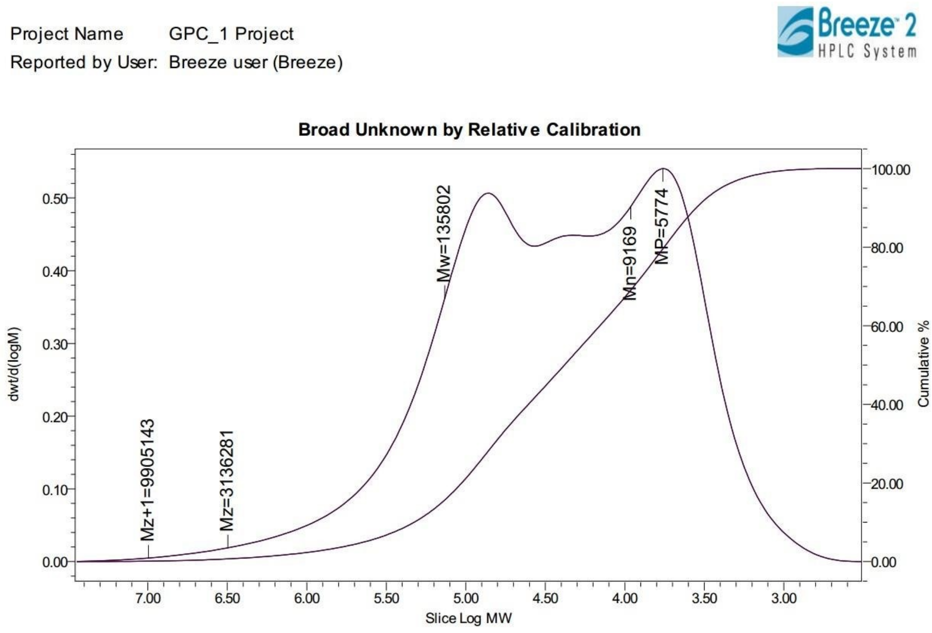


Figure 6. Gel permeation chromatography of copolymer (**TND-W**)

Polymer symbol	M_w	M_n
TND-W	135802	9169

Table 3. Molecular weight values of the prepared copolymer

4. Thermogravimetric Analysis (TGA/DTG)

This analysis seeks to assess the thermal stability of the copolymer synthesized in this work under the specified application conditions, which reach temperatures of up to 100°C. The copolymers exhibited excellent thermal stability at temperatures exceeding the designated application temperature for assessment. Thermal analysis is frequently employed to evaluate material behaviour under temperature fluctuations. Thermogravimetry (TG) is a widely used technique in thermal analysis that monitors variations in a sample's mass as it is heated. The resultant data is utilized to generate the derivative thermogravimetric curve (DTG), which offers a more comprehensive account of the weight loss rate. TG/DTG, commonly referred to as thermogravimetric analysis, is a crucial method for assessing the thermal stability and volatile constituents of a material. The approach functions by documenting weight variations in the sample while it is incrementally heated at a uniform rate. This analysis is typically conducted in low-oxygen conditions, using either air or inert gases such as helium or argon. A crucial element of the TG/DTG system is the thermobalance, an exceptionally sensitive scale that quantifies weight variations throughout the heating process [36]. The thermogravimetric analysis (TGA) of the produced copolymer indicated superior thermal stability, with degradation commencing at temperatures exceeding 200°C. The TGA/DTG thermograms presented in Figure 6 indicate that the copolymer experiences two separate stages of disintegration, occurring between 288–400°C.

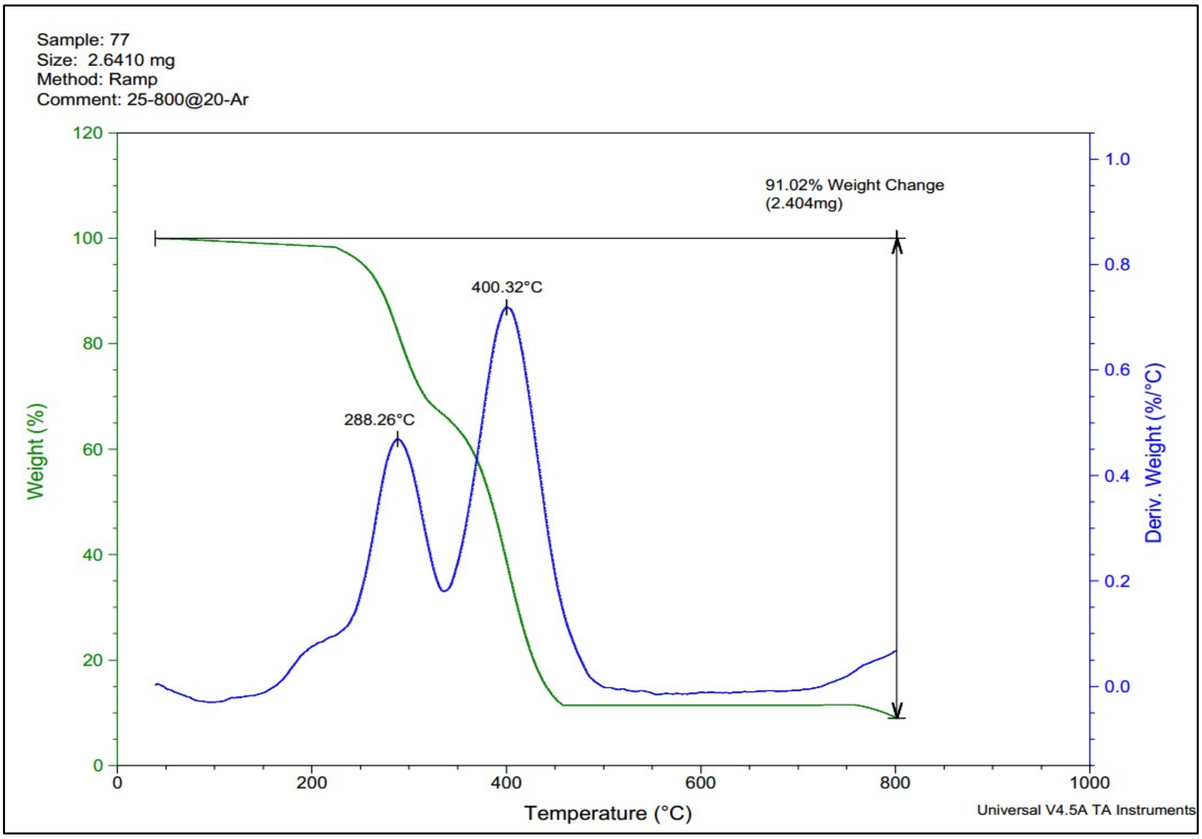


Figure 7. TG and DTG thermogram of copolymer (TND-W)

5. Investigating the Effect of Prepared Copolymer on the Rheological Characteristics of Lubricating Oil

Engine oil producers include polymers to sustain performance throughout the year. Nonetheless, these polymers may degrade under engine stress, resulting in diminished efficacy. The deterioration of viscosity index (VI) improvers and viscosity modifiers (VM) is contingent upon their chemical composition and external variables such as testing conditions, duration, and intensity [37], [38]. Investigating the impact of polymer additives on the flow characteristics of lubricating oil is crucial for sectors that depend on lubrication and machinery maintenance. The rheological properties of lubricant oil dictate its efficacy in minimising friction and facilitating seamless operation. Researchers examine shear stress-shear rate and viscosity-shear rate curves to comprehend the effects of viscosity enhancers for various principal reasons, including [39], [40]:

a. Assessment of Performance: Additives improve the viscosity-temperature correlation, and these graphs facilitate the evaluation of their efficacy under varying shear conditions [41].
b. Shear Stability: Guarantees the lubricant retains viscosity throughout time without degradation under stress [42].
c. Temperature Effects: Assists in determining the variations in viscosity at varying temperatures, which is crucial in extreme conditions.
d. Efficiency and Fuel Economy: Enhances lubricant compositions to improve engine performance and reduce friction.
e. Load-Bearing Capacity: Ensures the lubricant forms a protective coating to prevent wear under heavy loads.

f. Viscosity Classification: Facilitates the precise categorisation of lubricants according to standardised viscosity grades.
g. Quality Control: Verifies that lubricants conform to industry standards and fulfil client requirements.
h. Additive Development: Facilitates the design and optimisation of viscosity enhancers for targeted performance outcomes.
i. This research enhances the efficiency, durability, and performance of lubricants across diverse applications.

Analysing the (shear stress)-(shear rate) and (viscosity)-(shear rate) curves is crucial for a thorough assessment of the rheological behaviour of lubricating oil following the addition of viscosity improver additives. It enables researchers and manufacturers to optimise lubricant compositions to meet the demands of various applications and operating conditions, thereby enhancing machinery performance, extending equipment lifespan, and improving fuel efficiency.

A Brookfield rheometer was used to analyze the rheological properties of the base oil samples before and after the addition of polymer. Base oil samples were created by incorporating the manufactured copolymer (TND-W) at the optimal concentration of 10% by weight into the free additive oils (base 40 and 60) at temperatures of 40°C and 100°C. This study assessed rheological behaviour by analysing two types of flow curves: shear-rate against shear-stress curves and shear-rate versus viscosity curves [43].

6. Shear Rate and Shear Stress Flow Curve

Analysis of the data and flow curve of the base oil (40 and 60) combined with synthesised copolymer additives at varying temperatures, as presented in Tables (4)-(5) and Figures (8) to (11), clearly indicates that the oil samples exhibit characteristics akin to those of simple Bingham fluids. This performance closely mirrors that of the base oils devoid of additives, suggesting that the copolymer has not modified the Newtonian characteristics of the original oil. Instead, it has significantly augmented the oil's viscosity and stabilised it at extreme temperatures. This modification optimises the oil's characteristics and efficacy while diminishing friction under elevated temperature conditions [44].

Observing basic Bingham behavior in lubricant oil, especially when evaluating new polymer additions, is of utmost importance. It indicates the existence of a yield stress, marking the threshold at which the lubricant begins to flow and provides significant resistance to movement.[45]

The efficacy of synthesised polymers with lubricant oils (40 and 60) at temperatures of 40 and 100 °C is influenced by the polymer's structure, encompassing molecular weight, side chain length, and polarity.

rpm	**Shaer rate (Sec^{-1})**	**Temperature**	**Shear stress (dyne/cm^2)**	
			Blank	**Additive**
5	6.6	40°C	2.02	5.32
20	26.4		8.35	13.55

50	66		24.17	32.51
100	132		58.30	69.11
5	6.6	100°C	0.44	3.17
20	26.4		1.72	5.02
50	66		2.51	8.00
100	132		4.30	11.47

Table 4. Shear stress with increasing shear rate for lube oil (base 40) with copolymer additive (TND-W) at a constant concentration of 10% w/w

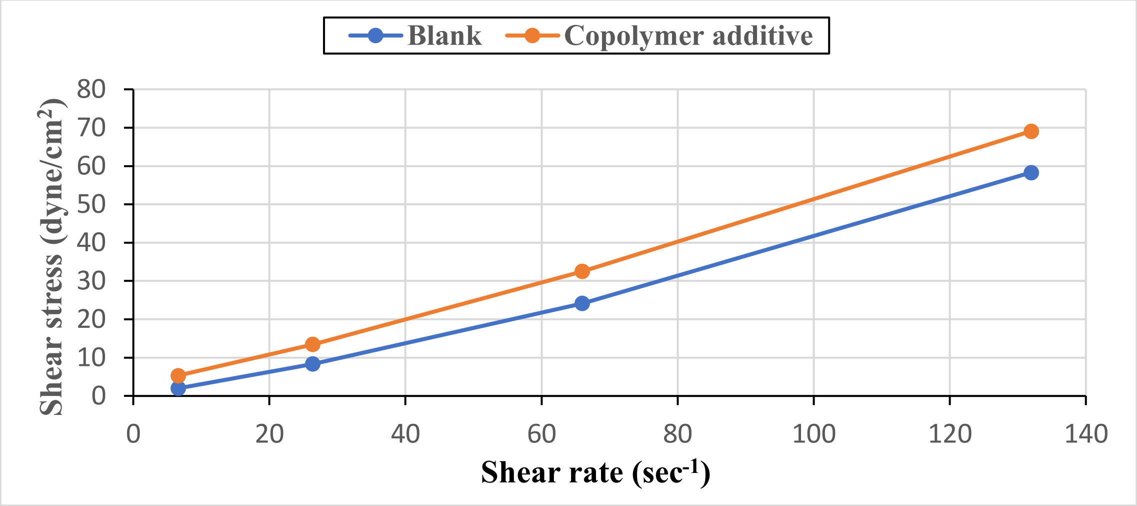


Figure 8. Flow curve of copolymer additive with 10 % concentration for lube oil (base oil 40) at 40 °C

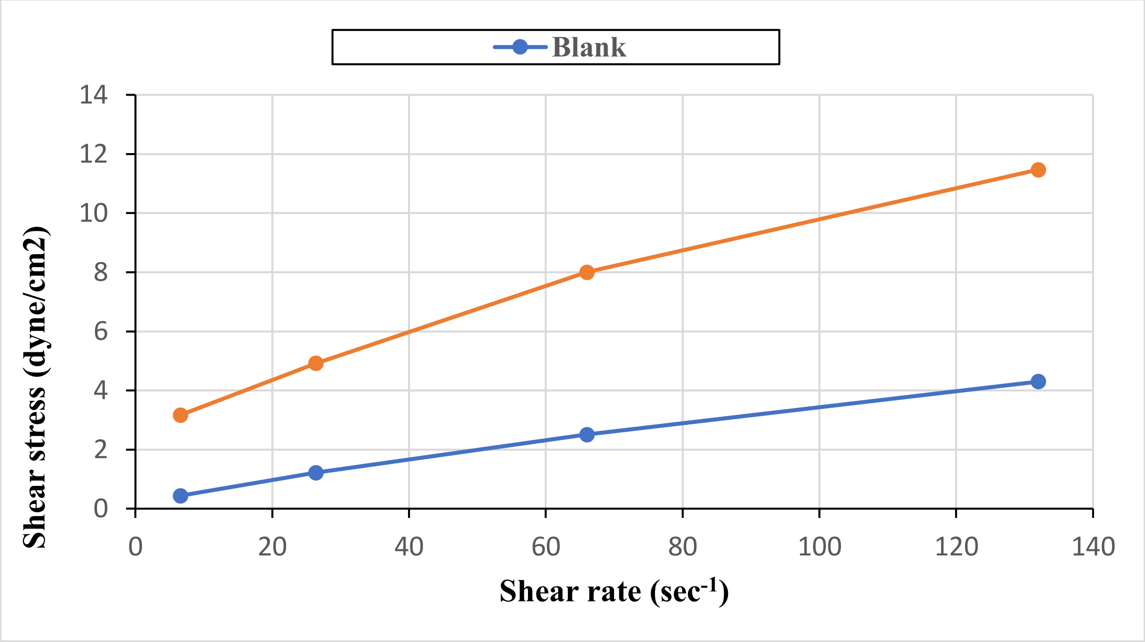


Figure 9. Flow curve of the copolymer additive at a 10% concentration in lubricating oil (base oil 40) at 100°C.

rpm	Shaer rate (Sec^{-1})	Temperature	Shear stress (dyne/cm^2)	
			Blank	Additive
5	6.6	40ºC	8.71	13.9
20	26.4		32.5	49.6
50	66		79.2	123
100	132		154	247
5	6.6	100ºC	1.45	4.26
20	26.4		4.80	9.24
50	66		11.5	22.7
100	132		21.1	43.4

Table 5. Shear stress with increasing shear rate for lube oil (base 60) with copolymer additive (TND-W) at a constant concentration of 10 %

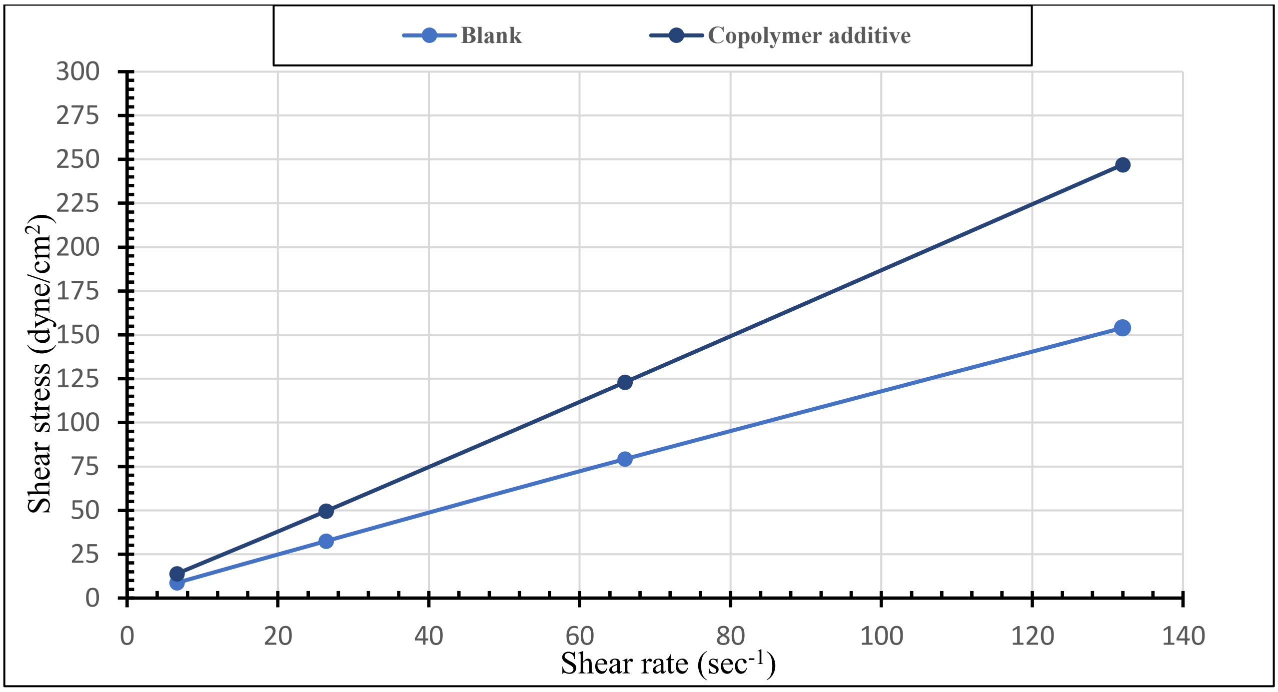


Figure 10. Flow curve of copolymer additive (TND-W) at (10%) w/w concentration with (base 60) and 40 °C

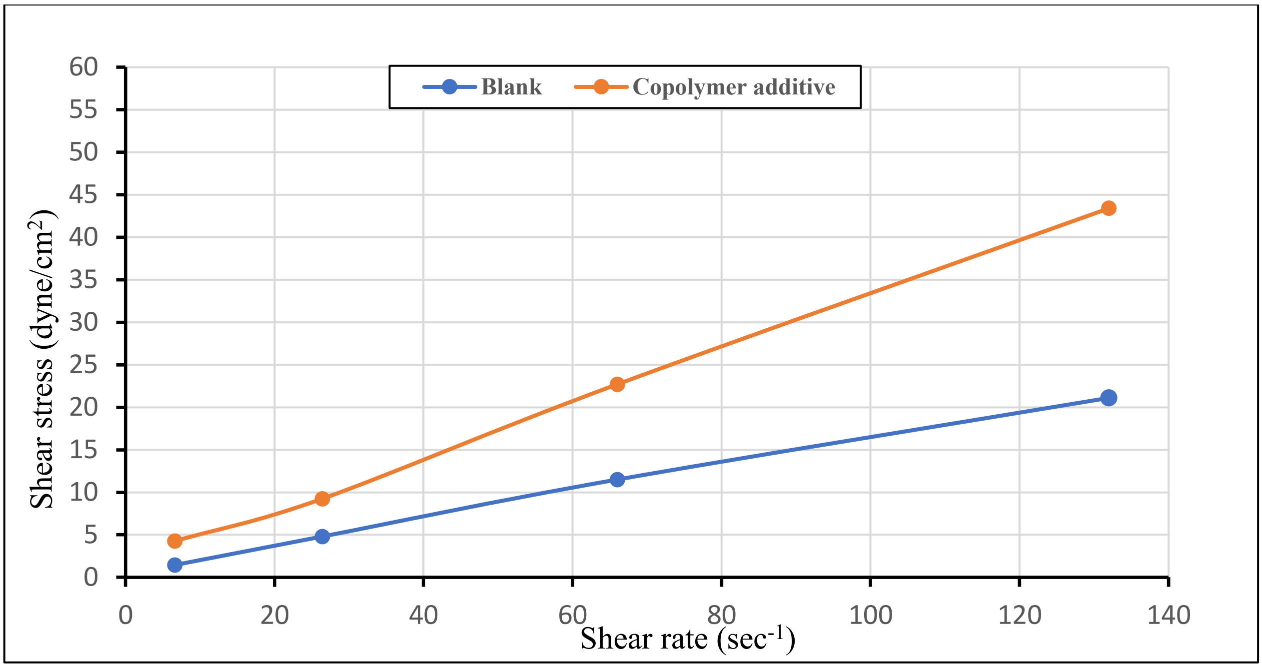


Figure 11. Flow curve of copolymer additive (TND-W) at (10%) w/w concentration with (base 60) and 100 °C

7. Viscosity Shear Rate Flow Curve

The analysis of the viscosity shear rate flow curve for lubricating oil combined with viscosity improver (VM) copolymer is a vital component of lubricant research and development. This study elucidates the impact of viscosity-improving polymers on the lubricant's performance under various shear conditions. It offers insights into the lubricant's viscosity behaviour at varying shear rates, especially in high-speed machinery and engines. Researchers examine these connections to enhance lubricant compositions, aiming for increased efficiency and reduced wear [46]. Furthermore, understanding the relationship between viscosity and shear rate is crucial for selecting the appropriate lubricant in various operational contexts, where fluctuations in temperature and speed can significantly impact lubrication efficacy. The investigation of viscosity-shear rate dependence facilitates the customisation of lubricants for particular applications, improving their effectiveness and prolonging the durability of essential machinery components [47], [48].

The apparent viscosity of each oil sample was measured using the same Brookfield rheometer at different temperatures (40°C and 100°C). The data are displayed in Tables (6) to (7) and Figures (12) to (15) for all samples. The data illustrated in the curve demonstrate a slight decrease in viscosity as the shear rate increases. Oil samples containing additives demonstrate weak non-Newtonian features under low shear rate settings, exhibiting shear thinning, which is characterised as pseudoplastic behaviour.[49] As the shear rate increases, the non-Newtonian behaviour diminishes, leading to the manifestation of Newtonian fluid features. This indicates that the formulated copolymer additive possesses the ability to withstand the decrease in oil viscosity, a phenomenon induced by shear pressures and temperature variations between 40°C and 100°C. The sample exhibited properties akin to those of a fundamental Bingham model.

The rheological properties of the synthesised polymers and the determinants influencing their efficacy as viscosity enhancers for base oils can be elucidated through an analysis of the shear stress-shear rate curves (Figures 8 to 11) and viscosity-shear rate curves (Figures 12 to 15) for each polymer at varying temperatures (40°C and 100°C). This comprehensive examination aims to elucidate the fundamental factors that can enhance polymer design for improved compatibility with base oils (40 and 60), a focus of ongoing research in this domain [26].

Figures (12) to (15) demonstrate the pronounced shear thinning behaviour of the synthesised copolymer in both categories of lubricant oils, indicating that the copolymer additive remains stable even under elevated temperatures and high shear rates.

The modification in the length of the hydrocarbon side chain and the number of oxygen atoms considerably influenced the enhancement or reduction of the efficiency of the synthesised copolymer with base oils. This impact is a crucial determinant of the overall performance and usability of polymeric materials. The structural alterations affected the interaction between the polymer and the base oil molecules, thereby modifying the effectiveness of the polymeric system.

rpm	Shear rate (Sec^{-1})	Temperature	Viscosity (cP)	
			Blank	Additive
5	6.6	40ºC	15.72	19.88
20	26.4		7.37	11.30
50	66		2.53	6.14
100	132		0.91	5.51
5	6.6	100ºC	3.54	6.47
20	26.4		2.00	4.87
50	66		1.21	4.00
100	132		0.52	3.78

Table 6. Viscosity with the increasing shear rate for lube oil (base 40) with copolymer additive (TND-W) at a constant concentration of 10% w/w

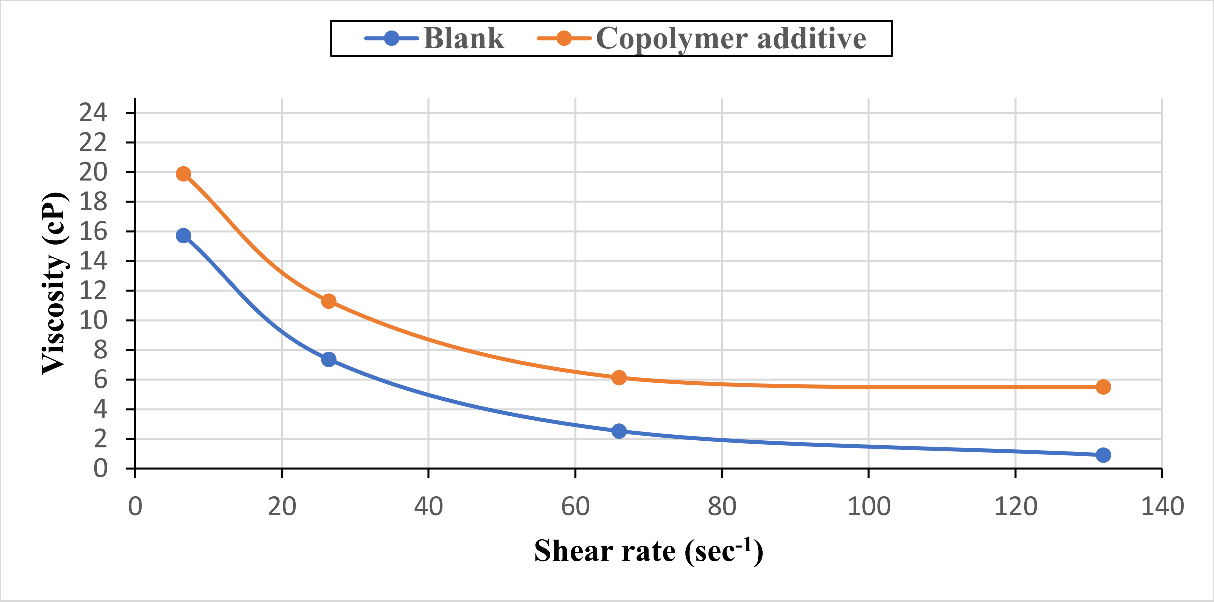


Figure 12. Viscosity - Shear Rate curve of (TND-W) copolymer additive at (10%) w/w concentration in (base 40) and 40 °C

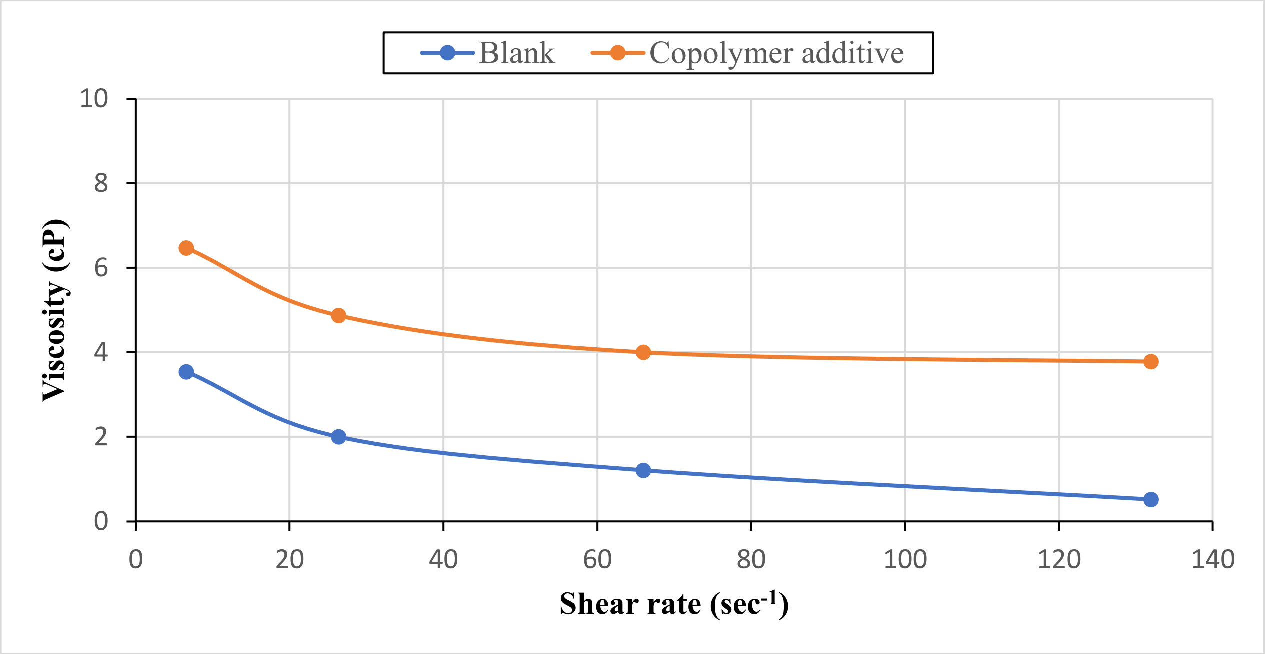


Figure 13. Viscosity - Shear Rate curve of (TND-W) copolymer additive at (10%) w/w concentration in (base 40) and 100 °C

rpm	Shear rate (Sec^{-1})	Temperature	Viscosity (cP)	
			Blank	Additive
5	6.6	40ºC	132	210
20	26.4		123	188
50	66		120	187
100	132		117	187
5	6.6	100ºC	22	64.5

20	26.4		18.2	35.0
50	66		17.4	34.4
100	132		16.0	32.9

Table 7. Viscosity with the increasing shear rate for lube oil (base 60) with copolymer additive (TND-W) at a constant concentration of 10% w/w

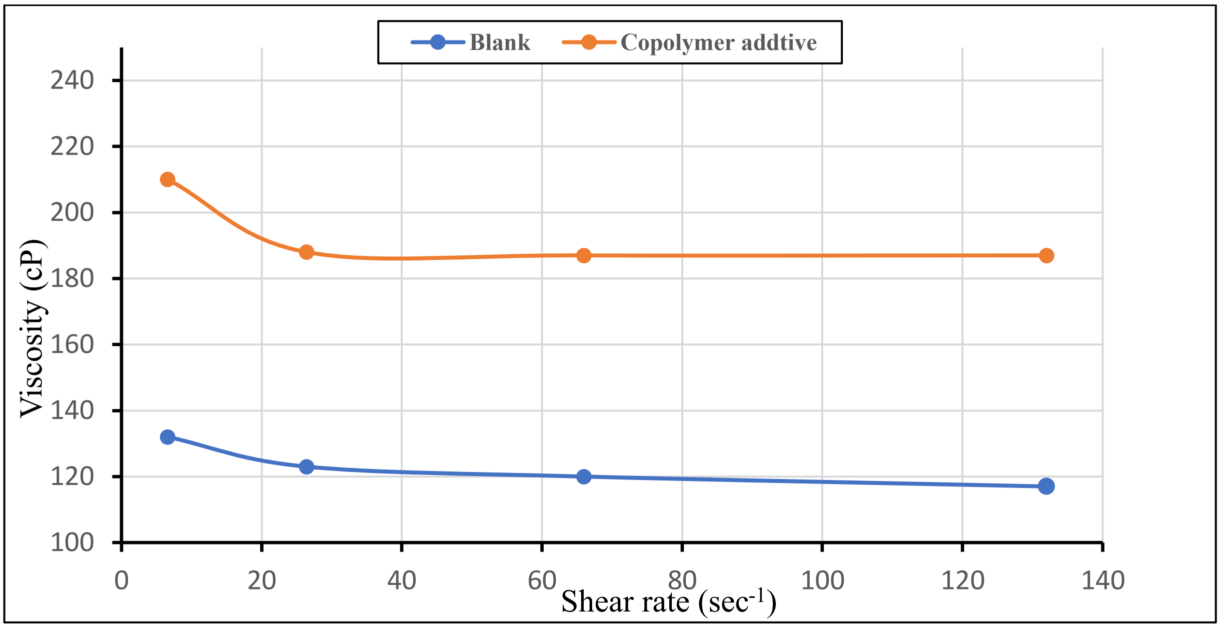


Figure 14. Viscosity - Shear Rate curve of (TND-W) copolymer additive at (10%) w/w concentration in (base 60) and 40 °C

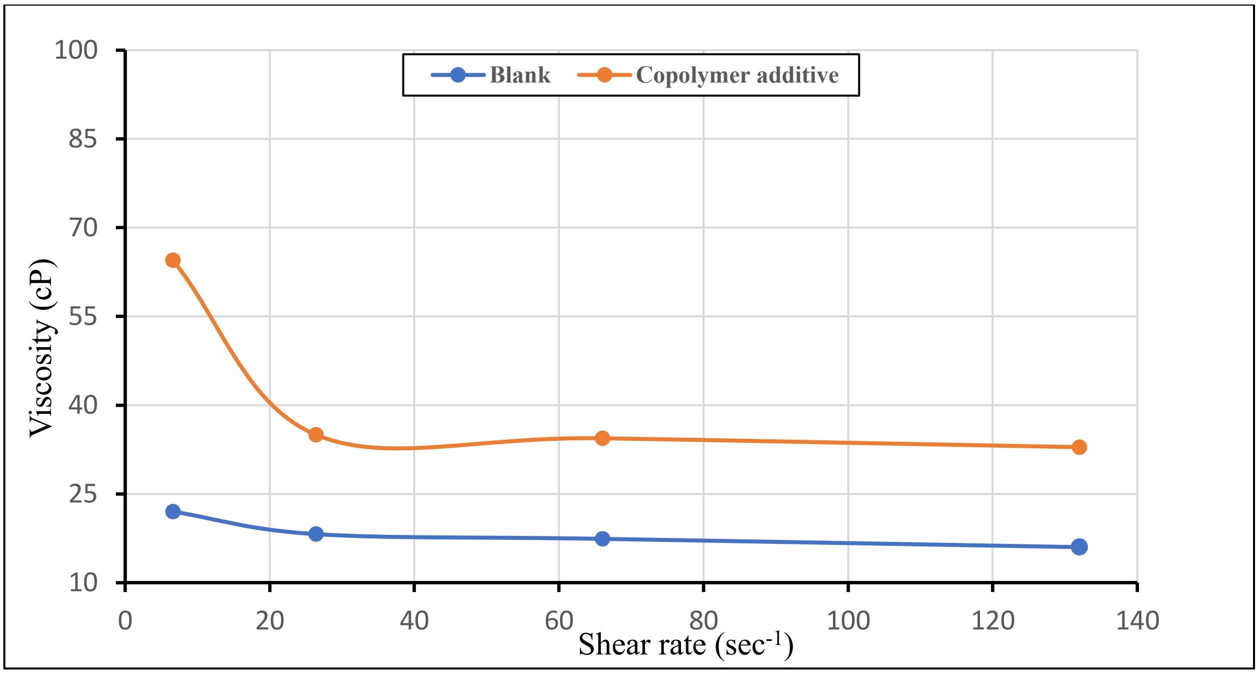


Figure 15. Viscosity - Shear Rate curve of (TND-W) copolymer additive at (10%) w/w concentration in (base 60) and 100 °C

8. Pour Point Depressant (PPD)

Pour point depressants (PPDs) are additives used in lubricating oils to enhance their performance in low-temperature environments. These additives are commonly utilised in base-oil lubricants formulated for situations with operating temperatures below 0°C. The influence of pour point depressants on the temperature at which wax crystals begin to precipitate, referred to as "cloud point," or the amount of wax that separates, is minimal [50]. These modifiers function as chemicals that adjust the dimensions of wax crystals by modifying their structure. This method is accomplished via co-crystallization with the precipitating wax. The molecular weight and structure of polymeric pour point depressants enable their efficacy across a broader range of temperatures. An efficient pour point depressant must possess particular structural attributes, including a comb-like configuration with elongated pendent groups, while eschewing excessive molecular weight that may hinder solubility at reduced temperatures [51].

Different concentrations of the synthesised copolymer (TND-W), ranging from 1000 to 5000 ppm, were evaluated for their efficacy as pour point depressants (PPD). Table 8 and Figures 16 and 17 demonstrate a favourable impact of pour point depressants at low concentrations. The copolymer (TND-W) demonstrated significant efficacy at a concentration of 4000 ppm by weight, reducing the pour point by -14 °C for base oil 40 and -12.5 °C for base oil 60. The oil's solvation capacity elucidates this phenomenon. The solvation capacity of any solvent decreases with a reduction in temperature and increases with a temperature rise. The diminished solvation capacity becomes increasingly evident as the molecular weight of the solute and its concentration rise [52], [25].

Concentration ppm	**Pour point °C**	
	Base oil 40	**Base oil 60**
Blank	-9 ± 0.070711	-5 ± 0.212132
1000	-6 ± 0.0212132	-6 ± 0.212132
2000	-7 ± 0.0282843	-6.5 ± 0.353553
3000	-9 ± 0.353553	-8 ± 0.2828243
4000	-14 ± 0.494975	-12.5 ± 0.141421
5000	-11 ± 0.141421	-10 ± 0.848528

Table 8. The correlation between the pour point and the concentration of copolymer additives (TND-W) in base oils 40 and 60. (The values are the ± SD)

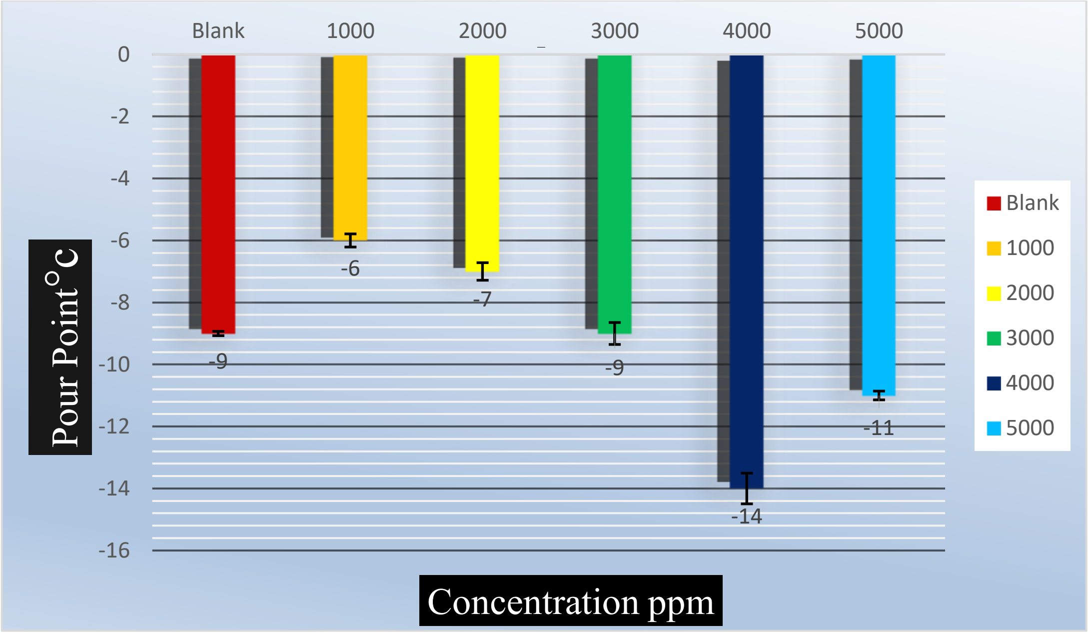


Figure 16. The concentration influence on pour point efficiency for copolymer additive (TND-W) in base oil 40

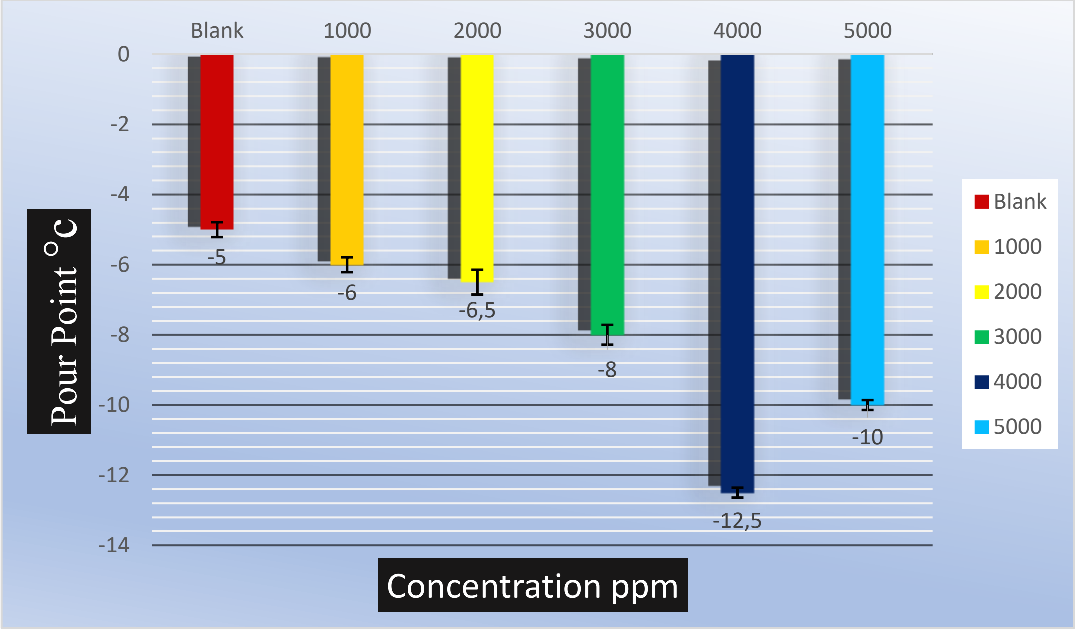


Figure 17. The concentration influence on pour point efficiency for copolymer additive (TND-W) in base oil 60

Conclusion

This study presents the evaluation of a novel copolymer (TND-W) as a pour point depressant (PPD) and viscosity modifier (VM) for lubricating oils. Using the ASTM D97 technique, the copolymer effectively reduced the pour point of the oils, although its performance diminished with increasing concentration due to decreased solubility in the lubricant, especially at lower temperatures. The highest reduction in pour point was achieved at a copolymer concentration of 4000 ppm. Additionally, dynamic viscosity tests conducted using a Brookfield rheometer revealed that the synthesized copolymer also functions as a viscosity modifier, improving the viscosity of lubricating oils without altering their core properties. The copolymer showed enhanced performance in modifying viscosity, particularly at elevated temperatures.

The flow behavior of the lubricating oil containing the copolymer was analyzed at 40°C and 100°C, showing that the oil exhibited characteristics of a Bingham fluid, indicating the significant influence of the copolymer on the oil's flow properties.

In conclusion, the TND-W copolymer is a promising dual-function additive that serves as both a pour point depressant and a viscosity modifier, contributing to the improvement of the flow and viscosity properties of lubricating oils, particularly in high-temperature environments.

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