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Influence of the Terpolymer and its Nanocomposite Pour Point Depressants on Lubricating Oil Properties

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Research Article

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Abstract

This work involves the investigation of the effect of structure variables of a new prepared terpolymer and its nanocomposite on the pour point depressant (PPD) and rheological behavior of lube oil. The terpolymer (TP) prepared by a free radical solution polymerization of the three monomers; alkyl acrylate (hexadecyl acrylate), diethyl maleate, and alpha olefin (1-hexadecene), but terpolymer nanocomposite (PNC) was synthesized by emulsion polymerization of the same monomers in presence of nanoclay (nano montmorillonite, NMMT). The entire prepared polymeric additives were characterized by FT-IR, ^{1}HNMR, DLS and GPC. The prepared polymers (TP & PNC) were blended with lube oil and measured the pour point temperatures (PPT), rheological properties and viscosity index (VI) before and after additives in detail. The results are encouraging and showing that, all polymeric additives exhibited a good efficiency as PPD, rheological properties and VII. The nanocomposite additive has a good efficiency more than conventional terpolymer for all tested techniques. The data were showed that, these additives can improve the properties of lube oil and this lube oil can used as engine lubricating oil.

Keywords: Wax; Pour point depressants; Lubricating oil; Terpolymers; Nanocomposites; Rheological properties

Introduction

Lubricating oil derived from petroleum involve a significant percentage of paraffinic waxes [1,2]. As the bulk oil temperature drops under its wax appearance temperature (WAT), the wax was precipitated then converted to wax gel with high yield strength, that encircles the internal area of the production pipelines [3,4]. The continuous precipitation of wax at the internal surface of these pipelines results in three stages of phase transformation [3,5]. At the first, the particles of wax aggregate in the oil clusters and by changing in

temperature and pressure, these oil clusters became sufficiently high to precipitate. At the second stage, the molecules of wax were shaped as a net or cage that mainly cause the oil to loss its fluidity [3,6]. At the end, with the continuous deposition of these cage leads to block the production pipelines that have to be brought to a halt. Briefly, the experiences of the oil and gas industry are in a major challenge to tackle this wax deposition [3,7,8].

To fix the problem, addition of pour point depressants (PPDs) is one of the economically successful methods that used to lower the pour point temperature of lubricating oils. Different types of polymers were researched and influenced as PPDs for improving the flowing properties of lubricating oils [1,9-11]. The efficiency of lubricating oils is often controlled by its rheological properties including the relation between viscosity and temperature. For example, to supply effective lube oils at both low and high temperatures, these oils should counterbalance the reduction in viscosity and thus diminishes the changes of viscosity with temperatures. The Properties of lubricating oils could have a great improvement by adding appropriate polymers that are called additives. These additives were doped with these lubricating oils to provide it valuable properties [12].

Classical polymeric additives used as flow improvers have part of disadvantages, where these additives have a lower effect on the elevated waxy crude oil and the microcrystalline wax, sensitive for the composition of crude oil and its properties and had lower time stability. So, these disadvantages do not reach all the transportation demands [13]. One of the fruitful methods that used for developing the polymeric additives is nanotechnology [14].

Over the past two decades, researches were concerned with evolving organic–inorganic nanocomposites because of their abnormal characteristics of the products produced. These nanocomposites were synthesized through dispersing extremely tiny quantities of the inorganic particles such as nanoclay into the polymeric matrix. However, the presence of these substances inside the polymer is restricted where they are completely different at their physical and chemical properties [15,16].

Nano-hybrid PPDs have become a new study focus in the field of enhancing the rheological characteristics of lube oils [17] where adding low-cost inorganic- organic polymer as PPD has taken significant attention [18-20]. Previous studies showed efficiency of the polymer nanohybrid to decrease the pour point temperatures of the oil more than the polymer alone where the nanohybrid modified the wax crystals morphology completely [18].

The present study aims to evaluate a new prepared terpolrmer (TP) and its polymer nanocomposite (PNC) as a nano-hybrid pour point depressant for lube oil. The prepared polymeric additives were purified and characterized by FT-IR, ^{1}HNMR, DLS and GPC. The thermal analysis for the prepared polymer and its nano-hybrid were measured by thermogravimetric analysis (TGA). The crystal morphology for waxy in lube oil with and without additives were observed by polarized optical microscopy (POM). The prepared products were evaluated as viscosity index (VI) and rheological properties improvement for lube oil according to ASTM D-975 standard.

Experimental Methods

Materials

The materials used in this paper, cetyl alchol (99%), methacrylic acid (≥98%), maleic anhydride (97%), 1-hexadecene (≥98%), Montmorillonite (MMT) nano-clay, hydroquinone, p-toluenesulfonic acid, benzoyl peroxide (99%), toluene, dioctyl sulfosuccinate sodium salt, anhydrous ethanol (≥99%)and sodium carbonate anhydrous were purchased from Sigma Aldrich Chemical Reagent Co., and used without additional purification. Lubricant oil was supplied by Co-operation Company (Egypt).

Synthesis of Hexadecyle Methylacrylate Ester

Hexadecyle methylacrylate ester (HDMAE) was prepared by reaction of methacrylic acid with cetyl alcohol using toluene as solvent, p-toluenesulfonic acid (PTSA) as catalyst and hydroquinone as protective agent for double boned. The reaction was performed in three necked flask having thermometer, nitrogen inlet and Dean–Stark with condenser where the water was collected by the help of Dean–Stark apparatus [10]. In a three-necked flask, alcohol, toluene and hydroquinone were added, and then elevate the temperature to 60 °C. After the alcohol has dissolved entirely, Methacrylic acid and PTSA have been added to the solution and heated gradually to reach 110°C for 8h. The reaction was stopped after separation of a theoretical amount of water. Prepared ester was cleaned several times with Na_2CO_3 aqueous solution (5 %) until the under layer became apparent then washed with distilled water. Finally, to

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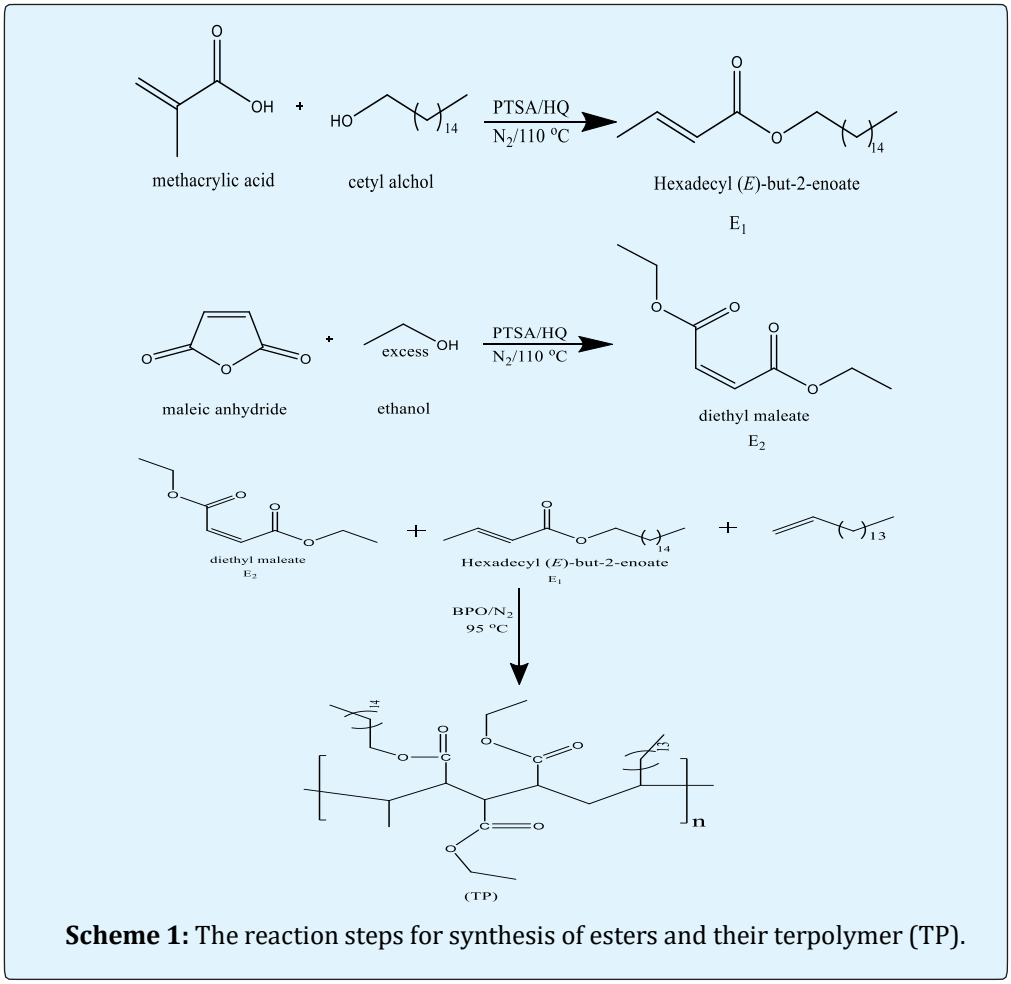
collect the prepared ester, distilled vacuum with a rotary evaporator and dried vacuum have been done [21].

Synthesis of Diethylmaleate Ester (DEME)

Diethylmaleate ester (DEME) was synthesized by reaction malic anhydride with excess of anhydrous ethanol, using toluene as solvent, p-toluenesulfonic acid (PTSA) as catalyst and hydroquinone as protective agent for double boned. The reaction was performed at three necked flask having thermometer, nitrogen inlet and Dean–Stark with condenser and the water was separated using the Dean–Stark [10,21]. In a three-necked flask, alcohol, hydroquinone and the solvent were mixed, and then elevate the temperature till reach 60°C. When the alcohol has entirely dissolved, the solution was supplemented with malic anhydride and PTSA and heated slowly until reach 110°C for 24 hr. The reaction ended when the theoretical amount of water has been separated. Prepared ester was cleaned several times with Na_2CO_3 aqueous solution (5 %) until the under layer liquid became apparent, and then washed with distilled water. Finally, to collect the prepared ester, distilled vacuum with a rotary evaporator and dried vacuum have been performed [21].

Synthesis of Terpolymer (THDMA-DEM-HD)

The synthesized esters (HDMAE and DEME) and 1-hexadecene were dissolved in the solvent (toluene) with molar ratio (1:1:1) in a three-necked flask having thermometer, nitrogen inlet and condenser [10]. The contents were initially subjected to twenty minutes of nitrogen flushing then elevate the temperature to 95 °C gradually. At this temperature, dissolved benzoyl peroxide was drowsily added as to the reaction. For 8 hours the entire content was refluxed. The final product was achieved with excess ethanol precipitated and vacuum-dried [10,22,23]. Scheme 1 showed the reaction steps.

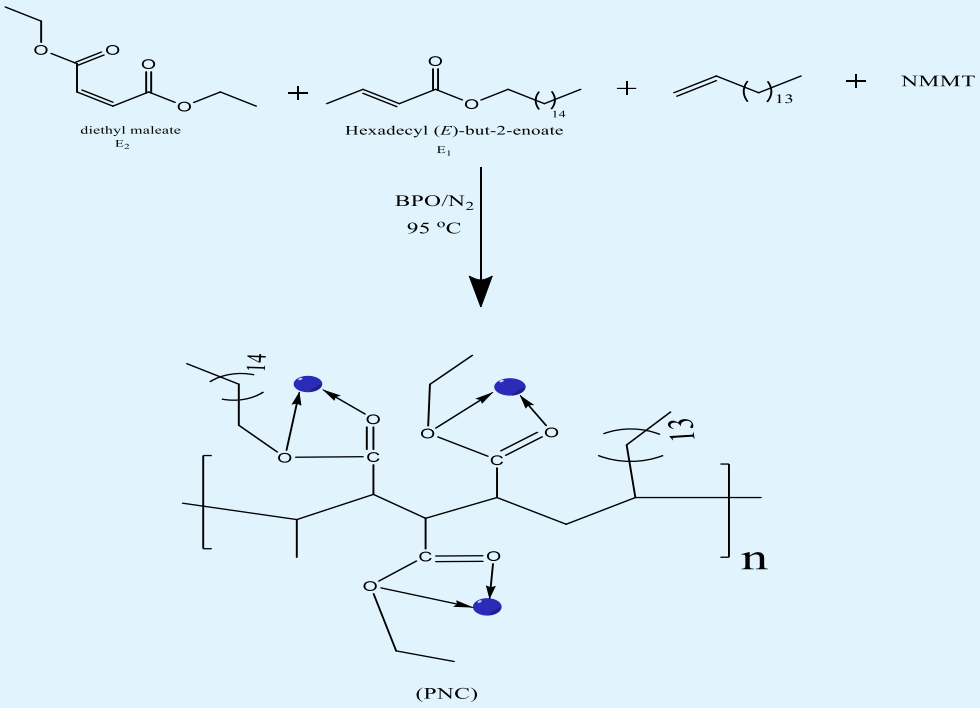


Scheme 1: The reaction steps for synthesis of esters and their terpolymer (TP).

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Synthesis of Terpolymer Nanocomposite (THDMA-DEM-HD/NMMT)

In this method the emulsion polymerization reaction was carried out in presence of nano clay. At the beginning, NMMT (1%) in distilled water was taken in a four-necked flask and stirred overnight and was sonicated for 30 min prior to polymerization. The monomers, DEME, HDMAE and HD were dissolved in toluene in a mol ratio (1:1:1) and dioctyl sulfosuccinate sodium salt are added to dispersed NMMT. After putting the mixture in the reactor, the system was purged with nitrogen gas for 15 min to remove the dissolved oxygen from the reaction medium. When the temperature of the reaction reached 95°C, the initiator was added to start the polymerization reaction [20,24]. The emulsion polymerization reaction was tack place for 24 h with a mixing speed of 450 rpm. After complete reaction, the system was cooled down to room temperature. The prepared terpolymer nanocomposites (THDMA-DEM-HD /NMMT) was collected. Scheme 2 showed the reaction steps.



Scheme 2: The reaction steps for synthesis terpolymer nanocomposite (PNC).

Characterization of the Prepared Additives

FT-IR (Fourier transform infrared) spectra were identified by a Nicolet iS10 (Thermo Scientific, USA) with resolution 1 cm^{-1} and wave number range 4000–400cm^{-1}. The samples were tested on potassium bromide (KBr) pellets.

^{1}HNMR (Hydrogen nuclear magnetic resonance) spectra were identified by using a BRUKER® Avance 400 MHz spectrometer that operated at 9.4 T and hydrogen observed at 400.13 MHz, in CDC13 (deutereated chloroform) solution and using TMS as an inner reference for chemical shifts of NMR.

Measurements size of the particles mainly depend on DLS (dynamic light scattering) that conducted by a Brookhaven Instruments 90 Plus model nanoparticle size/zeta potential analyzer (USA).

GPC (Gel permeation chromatography) determined the molecular weight of the prepared polymers in a Shimadzu LC10AD system has a refraction index detector. The analysis of the polymers was carried out by Tosoh TSH-Gel columns (Type H8). The analysis was done at 45°C with a mobile phase (THF (tetrahydrofurane)) at a rate of flow 1.0 ml/min.

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The wax crystal morphology of lube oil samples was identified by a DM2500P polarizing optical microscopy (Leica, Germany) at a cooling rate 0.8 C/min, and the images were captured at 0°C at a 100×magnification.

The pour point of the treated and untreated lube oil was determined by ASTM D-97 Standard. Viscosity, the most significant rheological parameter, heavily affects lube oil's cold flow properties. Temperature, however, also has a strong influence on viscosity [25]. An advanced rheometer (AntonPaar MCR302) was used to measure the viscosity-temperature curves of lube samples with a shear rate of 5 s^{-1} at different temperature from 25°C to 65°C.

Viscosity indexes (VI) of the pure lube oil and lube oil with additives were calculated according to ASTM D2270. The concentration at 10000 ppm was used to investigate the effect of the additive blended with lube oil on the Viscosity indexes. In this regard, the kinematic viscosity of the oil blended with terpolymer and terpolymer nanocomposite were recorded at 40°C and 100°C. The data were determined by taking an average of three results under the same conditions.

Results and Discussion

Characteristics of the Prepared TP and its PNC

FT-IR of TP and its PNC: FT-IR spectra of the terpolymer and its nanocomposite are presented in (Figures 1 & 2). The band at 1239 cm^{-1} represented the stretching vibrations of The C-O bond and the polymers displays stretching vibration peak for C=O of maleic anhydride at 1464 cm^{-1} and 1730 cm^{-1}, and C=O adsorption peaks of alkyl acrylate at 1730 cm^{-1}. The bands at 2929 cm^{-1} and 2853 cm^{-1} for C-H stretching vibration peak (for $-CH_2$ and $-CH_3$ respectively). However, the complete disappearance of C=C bands (at 1640 cm^{-1}), which confirmed the formation of terpolymer (THDMA-DEM-HD) [10]. The original Montmorillonite at figure 2 displays absorption peaks at 627 cm^{-1} for stretching SiO_2 and the asymmetric stretching vibration peak at 1150 cm^{-1} for Si-O-Si. The bands at 521 cm^{-1} and 461 cm^{-1} were the vibration bending of Si-O and Al-O-Si in MMT, respectively. From the above fully proved that NMMT had been successfully combined with terpolymer [26].

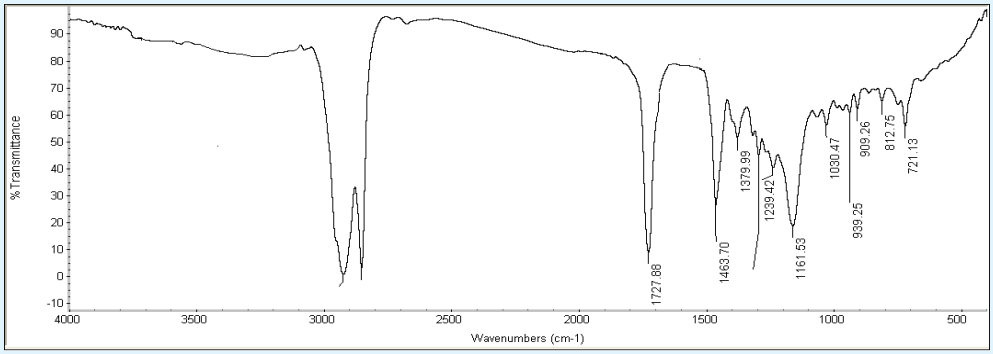


Figure 1: FT-IR spectrum for the prepared terpolymer (THDMA-DEM-HD).

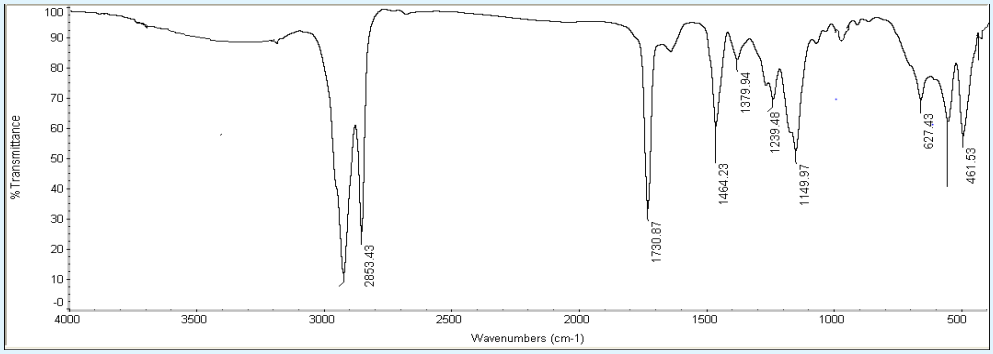


Figure 2: FT-IR spectrum for the prepared terpolymer nanocomposite (THDMA-DEM-HD/NMMT).

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^{1}HNMR of TP and its PNC: The ^{1}HNMR of the prepared terpolymer (TP) and polymer nanocomposite (PNC) are shown in Figures 3 & 4. The presence chemical shifts of all proton in the region 0.8 ppm and 4.3 ppm. The peak at 0.8 ppm was for the CH_3 protons, peak at 1.2 ppm was for CH_2 protons and peak at 1.6 ppm was for CH protons for alkyl groups. The peaks at region 1.96 – 2.37 ppm are for the COCH protons and the peak at 3.6 ppm for the $COCH_2$ of alkyl acrylate. The peaks at 4.13 - 4.3 ppm refer to the protons of alkyl ether (OCH).

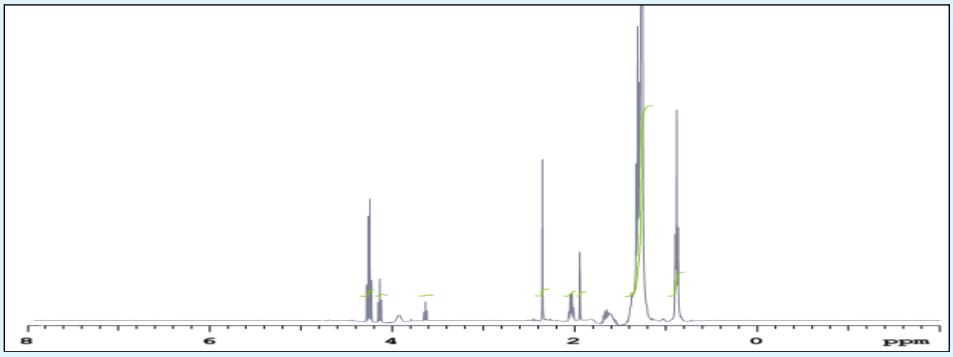


Figure 3: ^{1}HNMR spectrum for the prepared terpolymer (THDMA-DEM-HD).

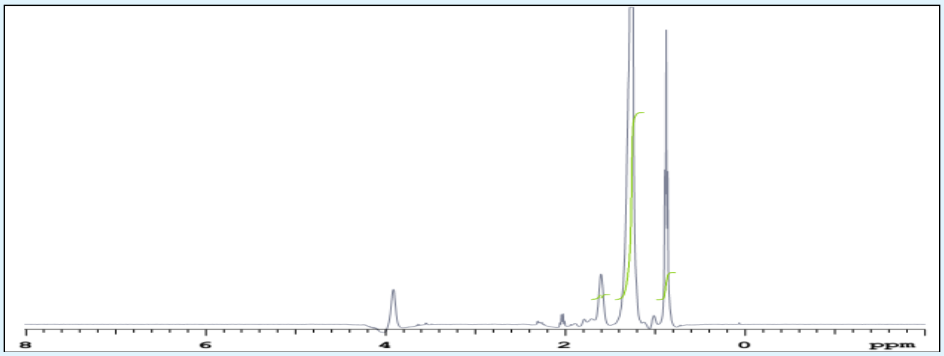


Figure 4: ^{1}HNMR spectrum for the prepared terpolymer nanocomposite (THDMA-DEM-HD/NMMT).

Dynamic Light Scattering (DLS) for Terpolymer Nanocomposite: DLS is a method which specifies the size of particles of distributed PNCs in a solution as shown in Figure 5. The synthesized PNC's size distribution profile had a particle size around 98.13 nm. The polydispersity index (PdI) was 0.208, indicating that the particles are naturally polydispersed.

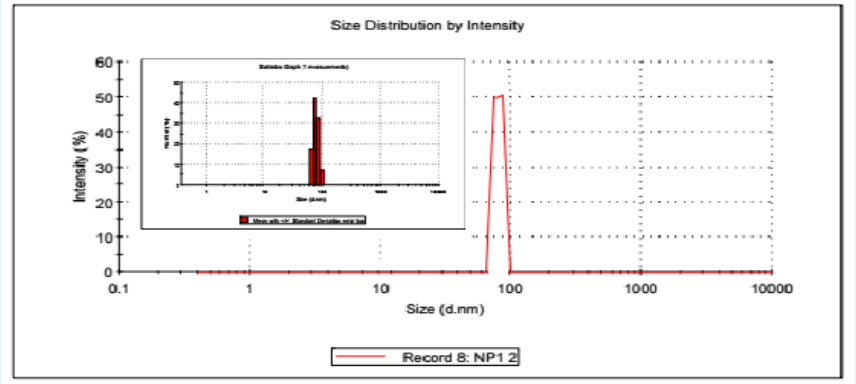


Figure 5: DLS spectrum for the prepared terpolymer nanocomposite (THDMA-DEM-HD/NMMT).

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Thermogravimetric Analysis (TGA) for the Prepared Terpolymer and its Polymer Nanocomposite: The thermal stability of the terpolymer (TP) and polymer nanocomposite (PNC) was assessed by thermogravimetric analysis under a nitrogen gas, given the thermograms that were shown in Figure 6. These thermograms of the samples have three decomposition stages. The first for TP was at range 25 -100°C with a weight loss of 30 %, and PNC was in the range 220 - 250°C with a weight loss of 20 %, attributed to water loss. The second degradation stages were differenced from one to other one, for TP was at 100 - 200°C with a weight loss 20 % but PNC degraded at 250 - 400°C with a weight loss 55 %. The last stage of TP was in the range of 400 – 600°C with a weight loss 50 % also for PNC was at 400 - 600°C with a weight loss 0.0 %. Accordingly, in the end of degradations the residual of TP was 0.0% but the residual of PNC was 25 %, which indicated that the PNC more stable than TP. This enhancement of the thermal stability of nanocomposites may be because of the pronounced thermal stability of MMT and the interaction between the MMT particles and the terpolymer matrix [27].

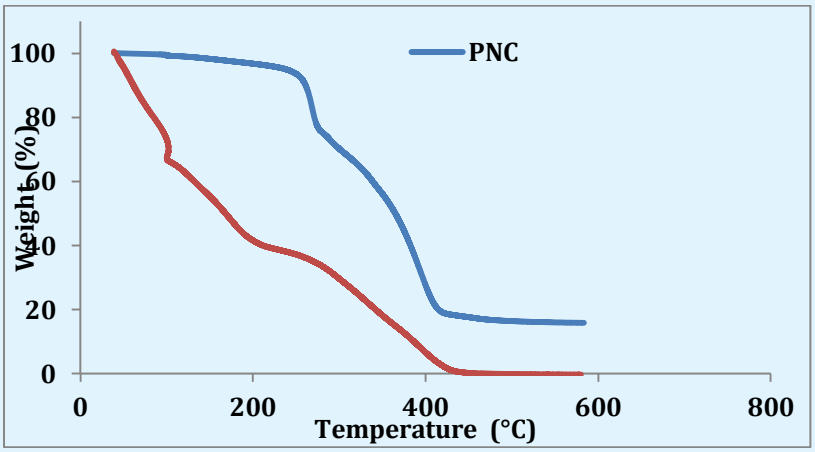


Figure 6: TGA for the prepared terpolymer and its polymer nanocomposite.

Effect of the Terpolymer and its Nanocomposite (TP and PNC) on the Pour Point

The pour point temperatures of the lube oil identified by blending the terpolymer and terpolymer nanocomposite additives at different dosages ranging from (3000 – 10000 ppm) with the lube oil then recorded in Table 1. The data showed that, the increasing in the concentration of the additives allow the pour point temperature to decrease. It is further observed (table 1) that polymer having nanoclay (NMMT) was more efficient than TP. Where, the PNC was depressed from 0.0 (pure lube oil) to -12 but TP depressed to -9 at 10000 ppm. At lower temperature, the nonpolar part (paraffin chains) of the polymer attracted towards the wax crystals of paraffin and prevents their crystal formation. On the other hand, the polar part (polar groups) of the polymer chains causes repulsion between waxy crystals and prevent the formation of waxy crystal network [28].

Polymer	$M_w \times 10^3$	Blank	3000 ppm	5000 ppm	10000 ppm
TP	82.1	0	-6	-9	-15
PNC	86.32	0	-12	-15	-21

Table 1: Results of pour point temperatures of pure lube oil and lube oil treated with additives at different concentrations.

Morphology Images by Polarized Optical Microscope (POM)

Figure 7 shows the morphology images by polarized optical microscope for wax crystals in pure lube oil and lube oil treated with 10000 ppm of TP and PNC at 0°C. Crystals of wax reflect polarized light and display bright white image.

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As shown in figures 7a-c, the shape, quantity and size of wax crystals varies across different samples. In the blank, Wax crystals are crystallizing, precipitating and agglomerating quickly this helps in forming colonies-shaped crystals of wax that had a structure as three-dimensional network with decreasing in temperature, thus losing the fluidity (Figure 7 a). Lube oil treated with 10000 ppm from TP or PNC showed forming of some tiny particle-shaped wax crystals (Figure 7 b & c). Wax crystal distribution is separated, regular, and has distinct size. Lube oil blended with PNC disperses more than lube oil with TP. Nano-hybrid (PNC) help in the modification of this phenomenon, where it allows the crystal of the wax to shaped smaller, more separated, more regular and uniform than TP.

This could be explained on two sides. Firstly, the wax crystallization of PNC offers heterogeneous nucleation sites [18]. The NMMT particles function as a nucleation point causing the wax crystallization formed tiny and uniform. This adversely affects the three dimensional (3D) net-work structure, enhancing the cold flow properties of lube oils. Secondly, NMMT has high surface energy; therefore crystallization must tend to be more compact for reducing the surface energy and interfacial area to preserve the system stable in energy when nanocomposite polymer (PNC) was blended to lube oils [25]. Many of liquid contained in the lube oil is produced from the 3D wax crystal network that significantly reduces interfacial area of the wax, thereby improving the cold flow properties of lube oil.

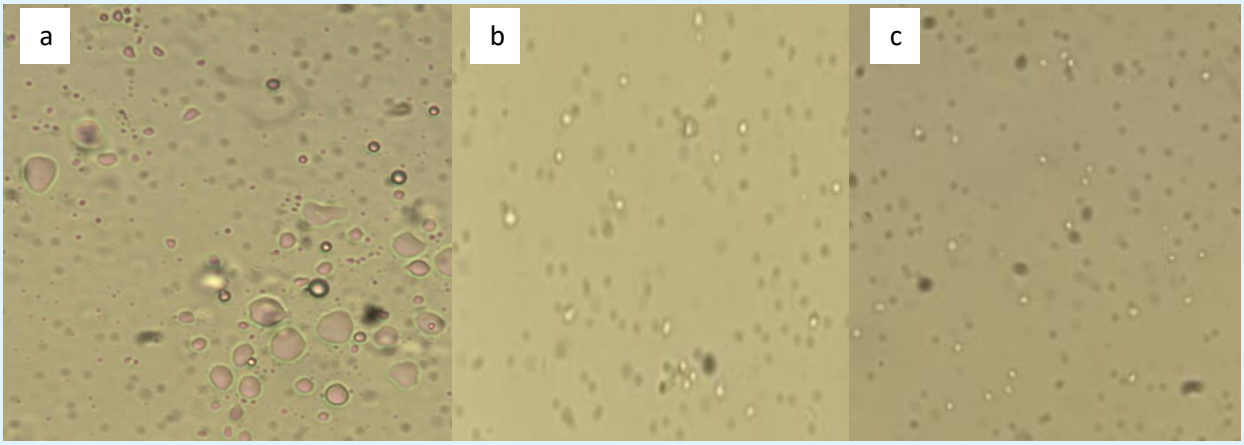


Figure 7: POM for a) Untreated lube oil, b) Treaded lube oil with 10000 ppm of TP and c) Treaded lube oil with 10000 ppm of PNC.

Rheological Properties and Flow Behavior

The rheological properties of the lube oil are heavily dependent on the shear rate, temperature, cooling rate, time of shearing and lube oil composition [21,29]. Flow properties of the lube oil without and with TP and PNC additives were established at the best concentration (10000 ppm) by dynamic measurements of the viscosity at 25, 45 and 65°C and plotted in Figures 8-13.

Figures 8-10, illustrate the relationship between shear rate against viscosity and show that the viscosity decrease with increasing shear rate and the viscosity of the lube oil additive were increase more than lube oil without additive at different types of temperature.

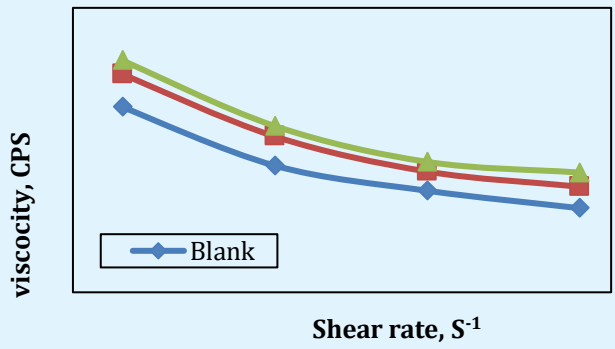


Figure 8: shear rate versus apparent viscosity of untreated and treated lube oil with 10000 ppm of TP and PNC at 25°C.

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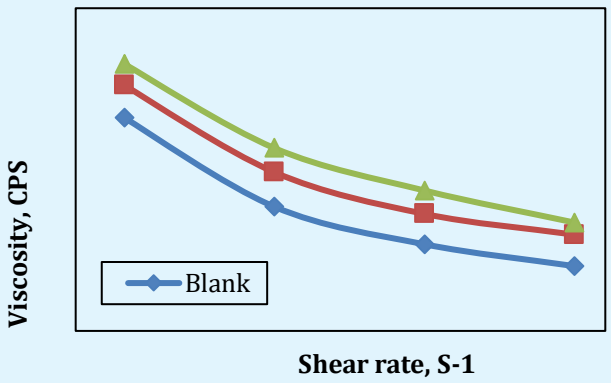


Figure 9: shear rate versus apparent viscosity of untreated and treated lube oil with 10000 ppm of TP and PNC at 45°C.

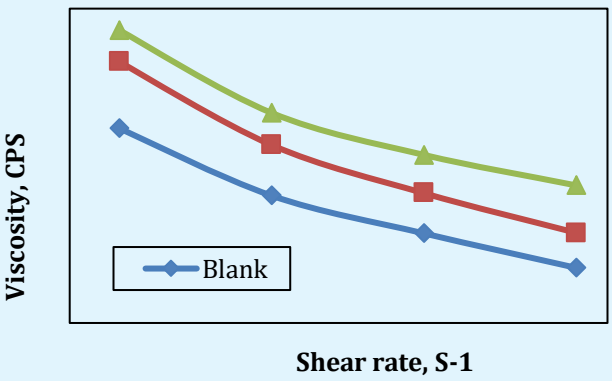


Figure 10: shear rate versus apparent viscosity of untreated and treated lube oil with 10000 ppm of TP and PNC at 65°C.

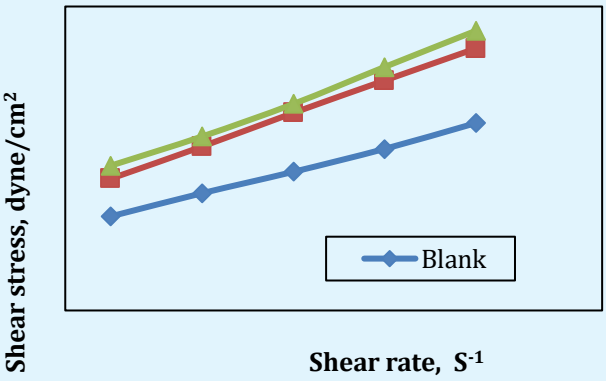


Figure 11: shear rate versus shear stress of untreated and treated lube oil with 10000 ppm of TP and PNC at 25°C.

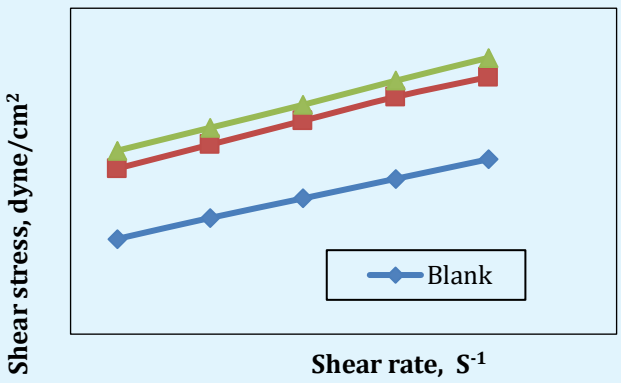


Figure 12: shear rate versus shear stress of untreated and treated lube oil with 10000 ppm of TP and PNC at 45°C.

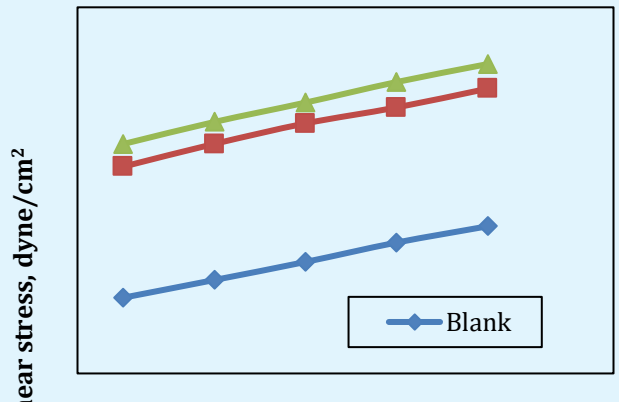


Figure 13: shear rate versus shear stress of untreated and treated lube oil with 10000 ppm of TP and PNC at 65°C.

However, the dynamic viscosity reduces as the shear rate increases till reach a limit value at high shear rate. This behavior could be clarified by increasing the shear rate, the agglomerates size decreases so some of the continuous phase in the agglomerates that was initially immobilized releases. With increasing the shear rate, the viscosity decreased till the agglomerates were broken entirely to the basic particles. The oxygen polarity of the ester group along the terpolymer and terpolymer nanocomposite chain played a role in prevention the crystals of the wax from agglomerating in lube oils [21]. The figures 11-13 illustrate the fitted experimental data of both shear stress and shear rate measurements according to the Bingham plastic model. The infinite viscosity of the

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shear rate is called apparent viscosity that obtained from the relation between shear rate and shear stress [29]. The obtained data of apparent viscosity and yield stress and correlation coefficient were determined for all tested lube oil at different temperatures and listed in Table 2. Overall, the model of Bingham has been shown a regular increase in values of apparent viscosity and yield stress of untreated and treated of lube oil samples with decreasing temperatures as shown in table 2. It shows that the values of apparent viscosity and yield stress of treated lube oil with TP and/or PNC were more than the values of untreated lube oil.

Samples	Temp., ˚C	Apparent Viscosity, cP	Yield Value, D/cm²	R²
Blank	25	1.251	378.1	0.999
	45	0.716	263.2	0.999
	65	0.463	145.6	0.997
TP	25	1.769	531.8	0.999
	45	0.833	474.8	0.998
	65	0.494	435.4	0.999
PNC	25	1.838	575.3	0.999
	45	0.840	526.1	0.995
	65	0.513	481.7	0.998

Table 2: The parameters of plastic viscosity and yield stress values of pure lube oil and treated lube oil by 10000 ppm from TP and PNC at different temperatures.

Evaluation of TP and PNC as Viscosity Index Improver on Lube Oil

A very significant role in lubricating oil production is the viscosity of lubricating oil. The kinematic viscosity of the lube oil without and with additives at concentration of 10000 ppm of the terpolymers and their nanocomposites was determined at different temperature 40 and 100°C. The data in Table 3 indicate that, the VI increase with additives more than without additives of the lube oil. With rising temperature the solvation power of the lube oil increases while its viscosity decreases. Due to increasing solvation power the polymer molecules swell or in other words its hydrodynamic volume increases. The enlarged hydrodynamic volume counterbalances the reduction in lube oil viscosity and thus diminishes the viscosity changes of additive doped lube oil [21]. The polymer nanocomposite (PNC) gives better performance as VII than terpolymer (TP) present in the lube oil. The entire terpolymer and polymer nanocomposite give better performance as VII in lube oil more than untreated lube oil.

Sample	Kinematic Viscosity, cP ASTM D-445		Viscosity Index
	40°C	100°C	
Blank	101.95	10.83	88.779
TP	102.97	11.19	93.394
PNC	99.524	10.97	94

Table 3: Viscosity index data of pure oil and lube oil treated with 10000 ppm.

Conclusion

The following findings can be reported from the above outcomes:

1. New terpolymer and its nanocomposite were fabricated, purified and characterized by different methods then investigated as pour point depressant and flow improver for the lube oil.
2. The terpolymer and its nanocomposite have a good efficiency as pour point depressant, rheological behaviors, viscosity index improvers and cold flow properties.
3. Polymer Nanocomposite solution is more stable and more efficient than terpolymer solution.

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