Comparative Study between a Copolymer Based on Oleic Acid and Its Nanohybrid for Improving the Cold Flow Properties of Diesel Fuel

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ABSTRACT: The as-synthesized copolymer based on the prepared monomers and its nanohybrid were used for improving the cold flow of diesel fuel that has a vital role in meeting energy needs. The copolymer (AE) was created using the prepared monomers, by free radical solution polymerization of the prepared hexadecylmaleamide and octyloleate ester, and the polymer nanohybrid (NH) was created by emulsion polymerization of the same monomers with 1% nano-SiO_2. The chemical structures of the copolymer and its nanohybrid were proved by Fourier transform infrared spectroscopy (FTIR), ^1H NMR, dynamic light scattering (DLS), and transmission electron microscopy (TEM). Through exploring the effect of the nanohybrid, before and after adding the dosage of the additives to the diesel fuel, the pour point

temperature (PPT), rheological characteristics, and viscosity index were measured. The data were the best for the nanohybrid; the PPT decreased from −3 to −36 °C upon adding 10,000 ppm nanohybrid but decreased from −3 to −30 °C for 10,000 ppm copolymer. In addition, the efficiency of the additives was proved by viscosity–shear rate and shear rate–shear stress curves to give the apparent viscosity, which decreased from 124 cP for the blank to 15.74 and 12.8 cP for AE and NH, respectively; also, the yield stress decreased from 576 D/Cm^2 for the blank to 541.44 and 477.9 D/Cm^2 for AE and NH, respectively, at room temperature. The viscosity index increased from 116 for the blank to 119 and 121 for the copolymer and the nanohybrid, respectively. Polarizing optical microscopy was performed to show more tiny and separated wax upon adding the additives. The findings showed that delayed crystal precipitation and altered crystal shape with the NH and AE greatly reduced low-temperature viscosity and enhanced the cold flow characteristics of the diesel fuel.
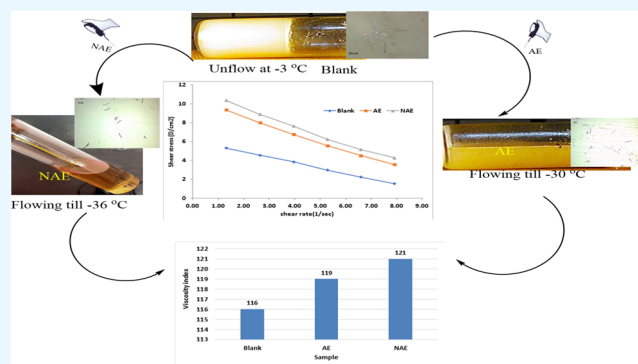
1. INTRODUCTION

Today, every nation in the globe is working really hard to get energy. Diesel fuel plays a crucial role in satisfying the demand in energy and is mostly used in a variety of commercial and industrial sectors as well as in the agriculture, our daily life, and other social spheres.[1−3] Wax crystals readily develop network architectures in diesel as the temperature decreases,[4−11] and the intense stacking of these crystals causes them to clog filters and negatively impact diesel flowability.[1,12−14]

The exceedingly diffuse wax deposition creates a serious operating issue. It alters the rheological characteristics (RP) of oil, causing an obstruction in the oil flowability. Wax deposition may occur when the physicochemical equilibrium conditions change as a result of a drop in temperature below the WAT. This causes wax crystals to grow and increase in viscosity, which eventually cause deposits to form on the pipeline wall, and high energy is needed to address the

problem of the dropping pressure resulting from the higher viscosity.[15−18]

Diesel crystallization creates challenges for storage, disposal, and transportation as well as billions of dollars in annual economic losses globally.[19−21] Therefore, because of its poor cold flow qualities, diesel's use and popularity are restricted.[1,22,23] Utilizing polymeric additives (PPD) is a cost-effective and environmentally friendly technique among the several methods (thermal process, mechanical methods, and also polymeric additives) used for improving the cold flow

of diesel.[1] The polymeric additives are used to improve the properties of the diesel fuel by decreasing the solid point and cold filter plugging point, improving the cold flow properties of the diesel fuel. This is realized by altering the behavior of the crystals by decreasing the formation of wax networks.[24,25] Alkyl methacrylate is a well-studied polymer used in diesel or oil,[26−28] EVA,[29,30] olefins,[31−33] and maleic anhydride polymers[34−36] and other types.[37−40] The alkyl with a long chain and groups with polarity is able to change the structure and shape of wax crystals. The efficiency of the polymeric additives might be enhanced by control over the ratio between the nonpolar chain and the polar groups.[41−43]

Nanotechnology has been used in many fields such as chemistry, physics, biology, medicine, engineering, and electronics and possesses high efficiency.[44] By spreading incredibly small amounts of inorganic particles, such as nanoclay, into the polymeric matrix, polymer nanocomposites were created.[45] Recently, these nanocomposites have been developed as a new type of pour point depressant for the petroleum industry, and they successfully lower oil's pour point and viscosity.[46] Yang et al.[47] compared poly(octadecyl acrylate) and its nanohybrid as a PPD; the findings from the study on the production of the nanocomposite as a PPD indicated that the nanocomposite had a better affinity for reducing viscosity.[44] As opposed to that, nanosilica was reportedly used in succession for nanosilica/polymer composition, to increase the thermal stability and mechanical strength. By formation of a high-strength precipitate and producing spherical templates for wax precipitation, the resultant nanohybrid PPD may reduce gelation and greatly increase the flowability of diesel fuel.[46,48−51]

This work aims to prepare a copolymer (AE) synthesized using the prepared hexadecylmaleamide (HDM) and octyloleate ester (OOE) by free radical polymerization. Additionally, its nanohybrid (NH) was prepared in the presence of 1% nano-SiO$_2$ using the same monomers via polymerization of an emulsion. The newly prepared AE and NH were used as a novel flow improver and pour point depressant for diesel fuel by applying them, and then, the copolymer and its nanohybrid were compared, which proved that the nanohybrid gave the best efficiency. Through detection, the beneficial properties of the recently synthesized polymers were confirmed of the pour point temperature (PPT),[52,53] viscosity index (VI),[54,55] and rheological characteristics (RP).[56] The ongoing preparation and primary function of the prepared polymer and its nanohybrid were affirmed via various instrumental analyses to show high efficiency.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Cetylamine $C_{16}H_{35}N$ (99%), oleic acid $C_{18}H_{34}O_2$ (98%), maleic anhydride $C_4H_2O_3$ (97%), 1-octanol $C_8H_{17}O$ (98%), nano-SiO$_2$, hydroquinone (HQ) $C_6H_6O_2$, p-toluene sulfonic acid (p-TSA) $C_7H_8O_3S$, benzoyl peroxide $C_{14}H_{10}O_4$ (99%), dioctyl sodium sulfosuccinate $C_{20}H_{37}NaO_7S$, and sodium hydroxide anhydrous NaOH were all purchased from the Sigma-Aldrich company. The solvents xylene, ethanol, and toluene were bought from Adwic Company. Co-operation Company provided the diesel fuel (Egypt), and its properties are listed in Table 1.

2.2. Synthesis of Hexadecylmaleamide (HDM). Maleic anhydride acid and cetyl amine were used to create HDM, with toluene (solvent) and *para*-toluene-sulfonic acid (p-TSA)

Table 1. Properties of the Used Diesel Fuel

property	method	result
density at 20 °C (kg/m^3)	SH/T0604	820.1
kinematic viscosity at 40 °C (mm^2/s)	ASTM D-445	3.35
flash point (°C)	ASTM D-93	55
pour point (°C)	ASTM D-96	−3
average carbon number (n)	IP 372/85 (GLC)	18.3
boiling distillate (°C)	GB/T258	283−379
acid value	GB/T258	1.96

(catalyst). To protect the double bond, hydroquinone was used. The reaction took place in a flask connected to a Dean Stark with a condenser; this Dean Stark was used to collect the exiting water.[44,45] Maleic anhydride (0.1 mol), hydroquinone (1% of acid), and toluene (50 mL) were sonicated at 60 °C. After entirely dissolving, cetyl amine (0.1 mol) and p-TSA (1% from total) were included in the process, and the temperature was steadily increased until it reached 120 °C; all of the system was under nitrogen gas. After a certain volume of water had been separated, the reaction eventually came to an end. To obtain the chemical in 87% yield according to Scheme 1, the as-synthesized HDM was cleaned repeatedly with NaOH solution (5%) until it became visible and then washed using distilled water and let to dry in a vacuum.

2.3. Synthesis of Octyloleate Ester (OOE). Octyloleate ester was prepared using the mixture of 0.1 mole oleic acid, 0.1 mole octanol, 50 mL of toluene, p-TSA, and HQ. The reaction was performed with the same previous steps until the OOE was obtained in 80% yield according to Scheme 2.

2.4. Synthesis of the Copolymer (AE). The polymer was prepared by free radical solution polymerization. The prepared HDM (0.1 mol) and OOE (0.1 mol) with benzoyl peroxide (1%) as an initiator in xylene as a solvent were taken in a flask with three necks, a thermometer, a nitrogen inlet, and a condenser.[47,57] The contents were first given a 20 min nitrogen flushing treatment before being progressively heated to 120 °C and then being completely refluxed for 8 h. The finished item was then separated using more ethanol to precipitate it and then dried.[58,59]

2.5. Synthesis of the Polymer Nanohybrid (NH). The polymer nanohybrid was synthesized through emulsion polymerization. Nano-SiO$_2$ in distilled water was stirred overnight at 45 °C in a three-necked flask. Subsequently, to achieve thorough dispersion of Nano-SiO$_2$ in solution, the mixture was sonicated for 20 min. The same monomers HDM and OOE were dissolved in xylene in a ratio of 1:1, while also dissolving the sodium salt of dioctyl sulfosuccinate in xylene and adding it to the dispersed solution. To get rid of any dissolved oxygen in the reaction liquid, the contents were first given a 20 min nitrogen flushing treatment before being progressively heated to 120 °C. Benzoyl peroxide was added as a consequence.[44,45] The emulsion polymerization process was run at 500 rpm for 12 h. Finally, the system was left to cool, and the nanohybrid (NH) was created by repeatedly washing the mixture to get rid of the used surfactant using the distilled water. The synthesis route of both the AE and NH is illustrated in Scheme 3.
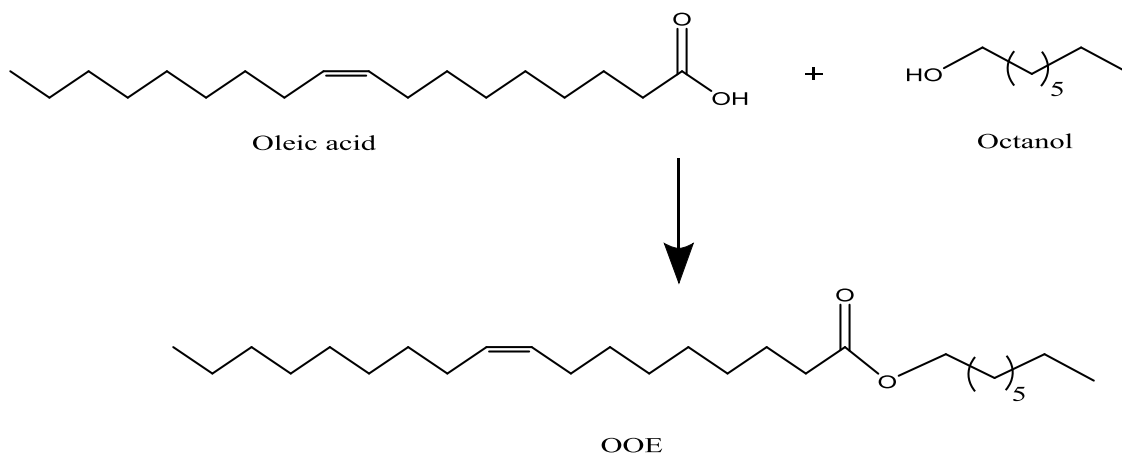
2.6. Characteristics of the Produced Polymer and Its Nanohybrid.

- Nicolet iS10 (Thermo Scientific) Fourier transform infrared (FTIR) spectra were recognized using 1 cm^{-1} resolution and a range of 400−4000 cm^{-1} of ν

Scheme 1. Synthesis of Hexadecylmaleamide (HDM)
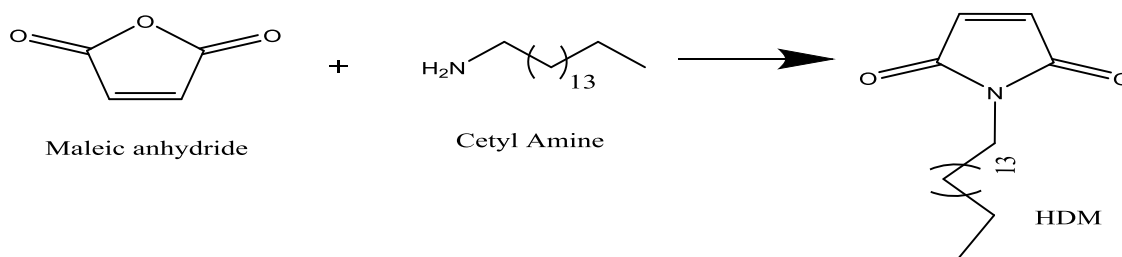
Scheme 2. Synthesis of Octyloleate Ester (OOE)

(wavenumber). The materials were examined using pellets of potassium bromide (KBr).

- ¹H NMR (proton nuclear magnetic resonance) was used to monitor hydrogen using deuterated chloroform as a solvent. A spectrometer (Bruker Avance 400 MHz) operating at 9.4 T was used. TMS was used as an inner reference for the shifts of the ¹H NMR.

- Dynamic light scattering or DLS (Brookhaven Instruments +90) was used to assess the size primarily.

- High-resolution transmission electron microscopy (HRTEM) (JEM2100LaB6, Japan) was used to accurately measure the nanoparticles' sizes at 200 kV voltage and with 0.14 nm resolution. Using an ultrasonicator, the solid sample was mixed with ethanol solution for HRTEM and then placed onto a copper grid that had been dusted with carbon. A Leica Ultracut UCT was used to perform ultra-cryomicrotomy on the nanohybrid sample before HRTEM analysis. Cryosections with a thickness of between 100 and 150 nm were made at a temperature of 150 °C using sharp glass knives with 45 cutting edges. The cross-sections were individually collected in sucrose solution and then supported on a dried copper grid with a size of 300.

- Using a DM2500P polarizing optical microscope (Leica, Germany), the wax crystal shape of diesel fuel samples was determined. Images were acquired by magnifying to 200 at 0 °C.

2.7. Evaluation of the Polymers. *2.7.1. As a Pour Point Depressant.* To detect the pour point of treated and untreated diesel fuel, the ASTM D-97 standard technique was used. After injecting the different concentrations of 3000, 5000, and 10,000 ppm of the additives, the PPT was measured at every 3 degrees and tested if the fuel still flows or not; when the fuel

freezes and is unable to flow, the PPT was detected to be the previous 3 degrees.

2.7.2. As a Viscosity Index Improver. The viscosity index (VI) of the diesel treated with the as-synthesized additives and that without treatment was determined (ASTM D2270). To examine the impact of the blended additive on the viscosity index, 10,000 ppm additive was utilized. In this regard, it was determined that the oil combined with the polymer and its nanohybrid had kinematic viscosities between 40 and 100 °C. Results were calculated by averaging three findings obtained under identical circumstances.

2.7.3. Study of the Rheological Behavior. The viscosity–temperature relationship of diesel fuel samples was observed using an advanced rheometer (Anton Par MCR302) connected to a cooling–heating system to adjust the temperature and then measure the rheological properties of the pure diesel fuel and that injected with the optimum concentration of 10,000 ppm AE and NH at different temperatures, 0, 15, and 25 °C, and a shear rate of 5 s⁻¹.

3. RESULTS AND DISCUSSION

3.1. Chemical Structure Characterization of the Prepared Polymers. IR (KBr, ν/cm⁻¹): 1370 cm⁻¹ (νN–C); 1756 cm⁻¹ (νC=O) for amide; 1647 cm⁻¹ (νC=C); 2859 cm⁻¹ (νCH₂), Figure 1, and 1460 cm⁻¹ (νC–O); 1738.44 cm⁻¹ (νC=O) for ester; 1645 cm⁻¹ (νC=C); 2926 cm⁻¹ (νCH₂), Figure 2; both figures confirmed the preparation of both monomers. Figures 3–5 show the preparation of the copolymer with the disappearance of 1650 cm⁻¹ (νC=C), with 3301 cm⁻¹ (νOH of silica), 1171 cm⁻¹ (νSi–O–Si asymmetry), 723 cm⁻¹ (νSi–O–Si symmetry), and 472 cm⁻¹ (νSi–O–Si bending), Figure 4, proving the formation of the nanohybrid, and after the matching between the IR values

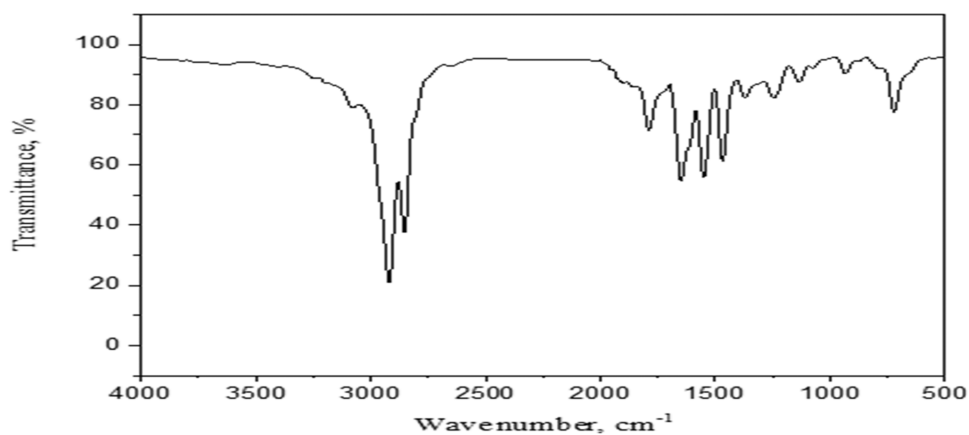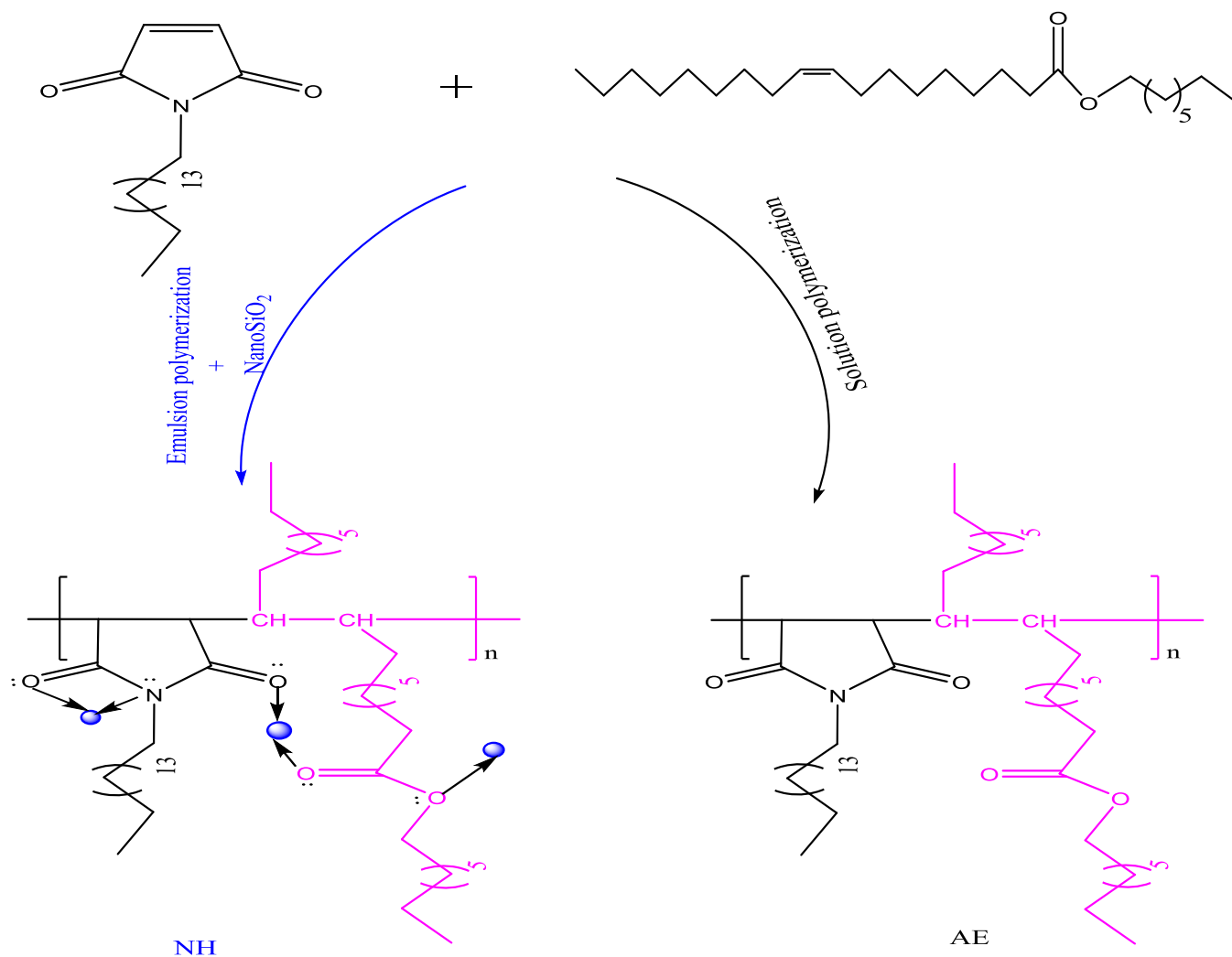**Scheme 3. Synthesis of Both the Copolymer (AE) and Polymer Nanohybrid (NH)**

Figure 1. IR spectrum of hexadecylmaleamide.

(KBr, ν/cm^{-1}) for the compounds AE and NH, it was noticed that matching reached 99.1%, as shown in the figure.[60]

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.7−0.8 (trip, 3H, CH$_3$), 1.1−1.3 (5-5-methine 5−13 CH$_2$), 2.4−2.3 (4 s.CH succinimide), 3−3.9 (methylene CH$_2$) as shown in Figures 6 and 7.

Figure 8 displays the **DLS** pictures for an example sample of the nanohybrid (NH). The findings clearly show that the size

distribution profile comprised particles with sizes between 80 and 100 nm, which support the production of nanohybrid (NH) materials. The DLS is detected to measure the size of particles of the nanohybrid polymer, as shown in the figure, giving 89 nm in the scale of the DLS image, proving the composition of the nanohybrid.

The **HRTEM** analysis image of the polymer nanohybrid (NH) is shown in Figure 9. The dispersion of the nanoparticles
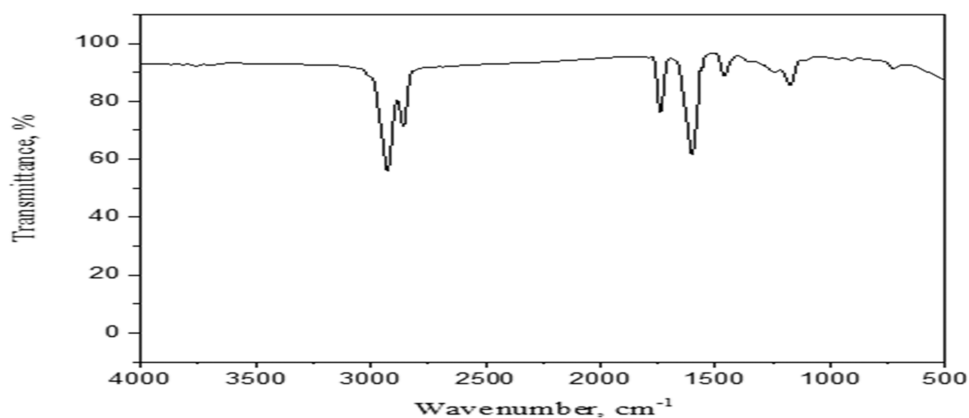
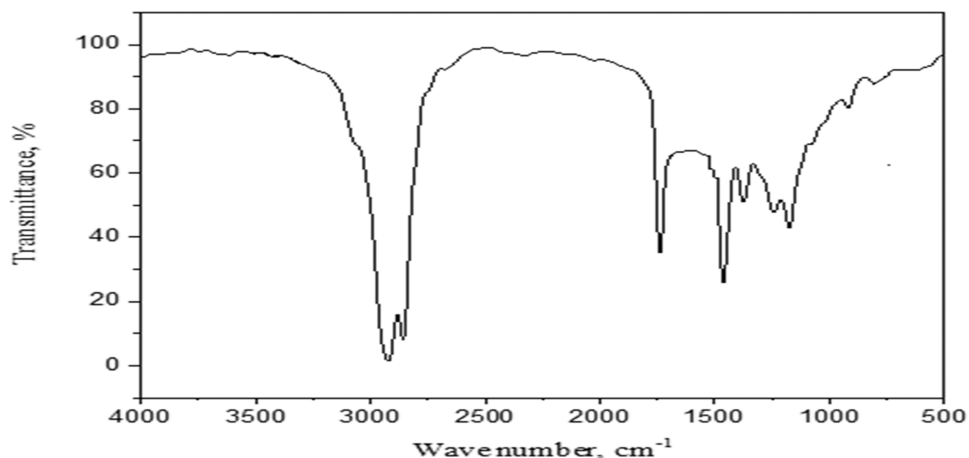**Figure 2.** IR spectrum of octyloleate ester.

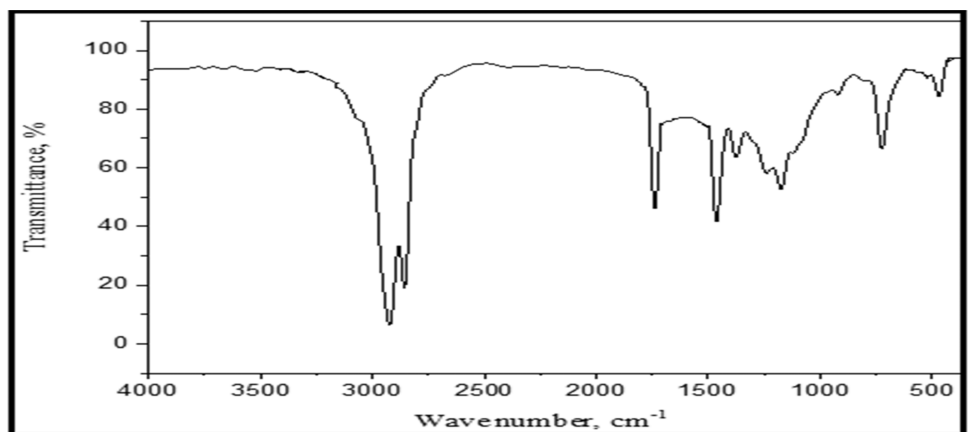**Figure 3.** IR spectrum of the copolymer (AE).

Figure 4. IR spectrum of the polymer nanohybrid (NH).

of nano-SiO$_2$ in the polymer is clear in the TEM image, where the huge part with the dark color represents the polymer itself and the white dots represent the nano-SiO$_2$.

The wax crystal morphology is shown in Figure 10. An accumulation of wax crystals in the blank was observed; the added additives absorbed on the wax crystal and changed the morphological structure, inhibiting the accumulation of wax crystals.

3.2. Pour Point Temperature (PPT). The effect of the prepared polymer and its nanohybrid in lowering the pour point temperature (the lowest flowing temperature of the oil)

can be demonstrated by the fact that at low temperatures, the wax crystals were attracted to the nonpolar chains of the polymer, preventing the formation of wax networks; at the same time, the polar groups acted primarily in repulsion between the wax chains, ultimately preventing the formation of wax networks.[44,52,53]

The findings are given in Figure 11 and Table 2; pour point temperatures were measured by treating diesel fuel with AE and the NH at various doses (3000, 5000, and 10,000 ppm). The findings demonstrated that the increase in the additive content resulted in a notable drop of the pour point
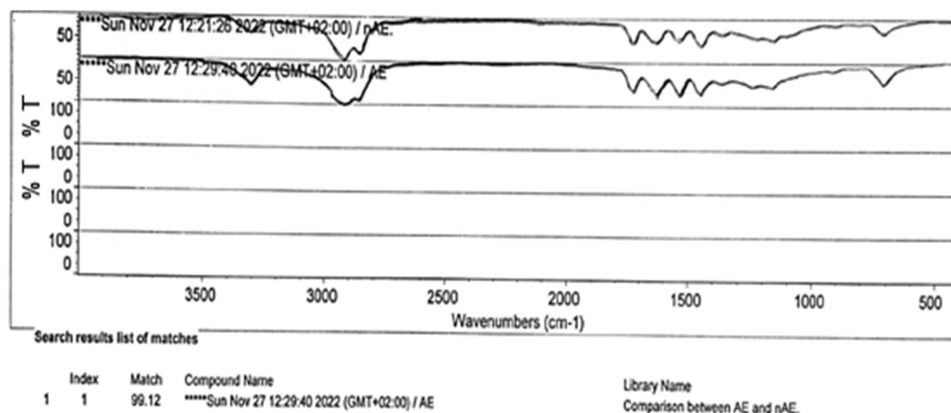
Figure 5. IR spectrum matching between the copolymer (AE) and polymer nanohybrid (NH).
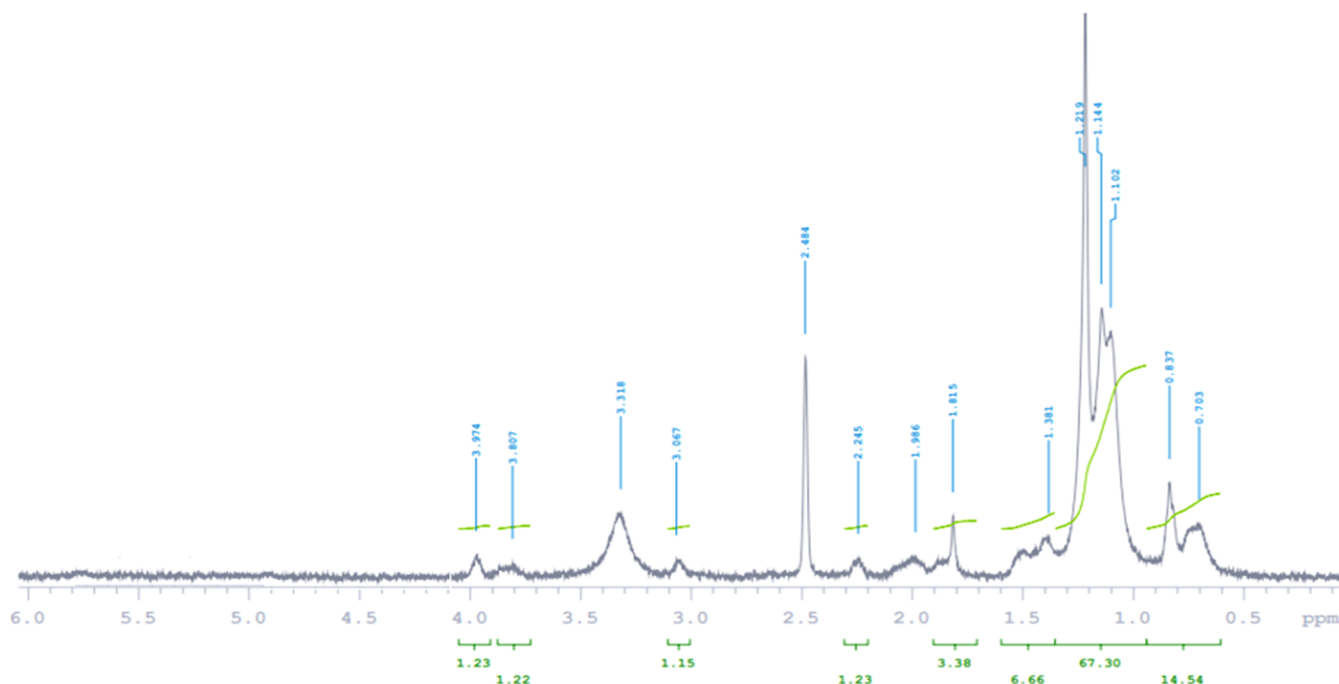

Figure 6. ^{1}H NMR spectrum of the prepared copolymer (AE).

temperature. Further research revealed that the NH was superior to AE in diminishing the pour point temperature. Diesel fuel is cooled by combining 10,000 ppm AE and NH, separately, to reduce its temperature from −3 °C (blank) to −30 and −36 °C, respectively.

3.3. Viscosity Index Improver. Oil's viscosity is its most crucial quality. The solvation power of diesel fuel increased with the increase in the temperature, but the viscosity of the fuel dropped. The polymer molecules were swollen, or to put it another way, their hydrodynamic volume was enlarged, as shown by the increase in solvation power. The viscosity of diesel fuel was reduced because the increase in hydrodynamic volume offsets the decline in viscosity.[61]

At 40 and 100 °C, the kinematic viscosity of diesel fuel was monitored both with and without the addition of AE and NH at a concentration of 10,000 ppm. The findings are presented in Figure 12. The findings showed that AE and NH treatments for diesel fuel increased the viscosity index (VI). The findings of comparing the effectiveness of the AE and NH as diesel oil additives by observing their impact on the values of viscosity

index (VII) revealed that VI was calculated to be 116 for a blank sample of diesel fuel as shown in Table 3. On the other hand, treatment with AE or NH, which produced more VI than that of the untreated diesel fuel may better act as VII. The predicted VI is greater when using NH (121) than with AE (119). After repeating the method more than once, it was found to be reproducible, indicating that the results were accurate.

3.4. Rheological Behavior. The key factors affecting the rheological characteristics of diesel fuel are shear rate, temperature, cooling rate, period of shearing, and oil content.[62,63] The term apparent viscosity, which comes from the literature, refers to the viscosity's dependence on the shear rate.[62] This indicates that the aggregation of wax masses causes the viscosity to drop when the shear rate is increased.[62] Figure 13a−c depicts the relation between the shear rate and the viscosity of untreated and treated diesel fuel with 10,000 ppm AE and NH at 25, 15, and 0 °C as well as the relationship between the shear rate and shear stress of untreated and

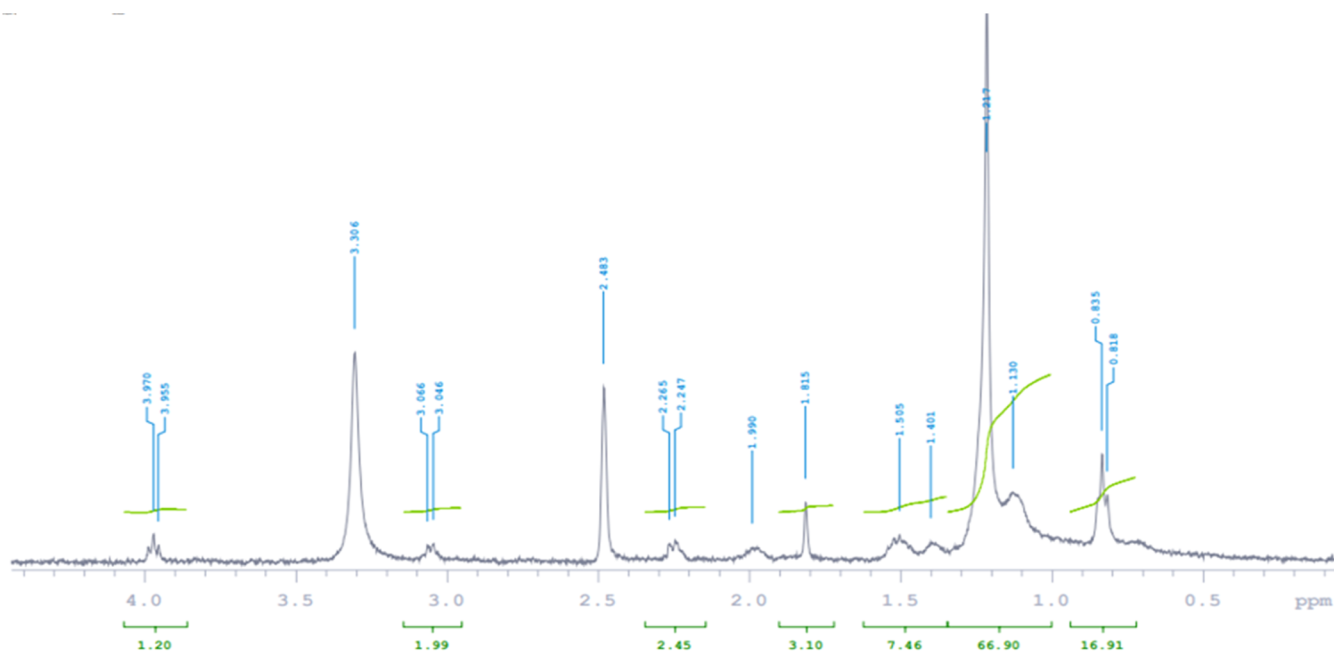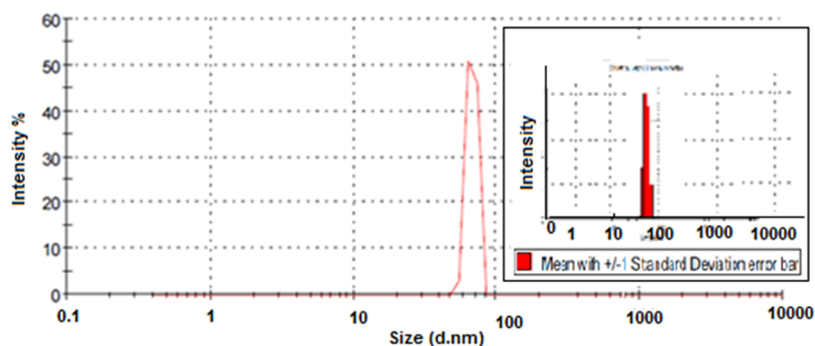**Figure 7.** ^{1}H NMR spectrum of the polymer nanohybrid (NH).

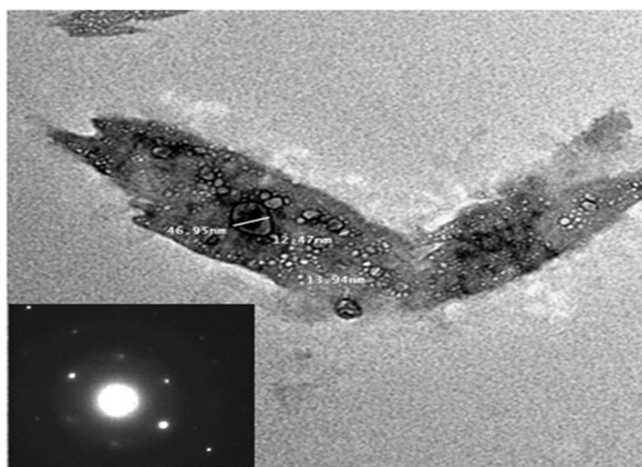**Figure 8.** DLS images of the polymer nanohybrid (NH).

Figure 9. HRTEM analysis image of the polymer nanohybrid (NH).

treated diesel fuel at 25, 15, and 0 °C, as illustrated in Figure 14a−c.

From Figure 13a−c, one can note that the viscosity decreases with increasing shear rate and also decreases with increasing temp. However, on comparison of the viscosity of the diesel fuel treated with the additives with that of pure diesel fuel, one could note that the viscosity decreases with the addition of the additives. This phenomenon, called shear thinning, can be explained through increasing shear rate, which reduces the waxy agglomerates and causes part of the continuous phase that had been immobilized within the agglomerates to be released.[64] In all studied samples, particularly at high temperatures, the viscosity reduces roughly linearly with the increase of the shear rate.[65] In the oils, wax crystals tend to aggregate, but this is prevented by the strong polarity of oxygen in the ester group along the polymer chain.[66]

Treating diesel fuel with AE or NH and increasing the shear rate lead to a decrease in the viscosity, where at a shear rate of 382 s^{-1}, the viscosity was 387 cP, but after injection of the samples (AE and NH), the viscosity becomes 182 cP and 114 cP, respectively, at 25 °C. The curve of the shear stress is linear, where the shear stress is sharply decreased upon treating the diesel fuel with AE or NH. The parameters plastic viscosity and yield stress were also detected and are listed in Table 4. From the listed data, it was observed that diesel fuel has non-Newtonian behavior in both cases of treated or untreated.[63] The apparent viscosity (η_{app}) of the diesel fuel injected with AE or NH was decreased, where the η_{app} was decreased from
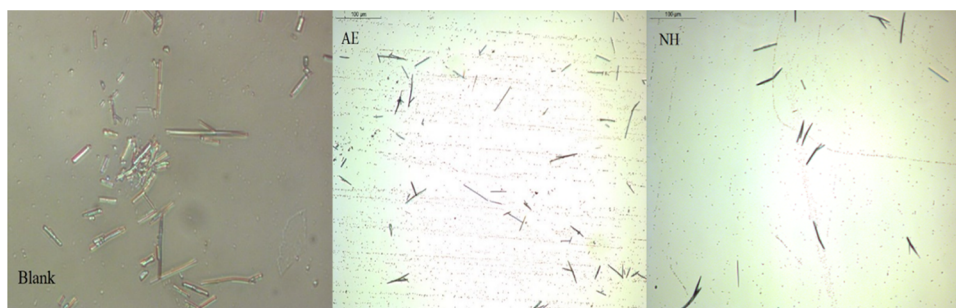
Figure 10. Polarized optical microscopy image of the wax of diesel fuel samples [blank, with the prepared copolymer (AE), and with the polymer nanohybrid (NH)].
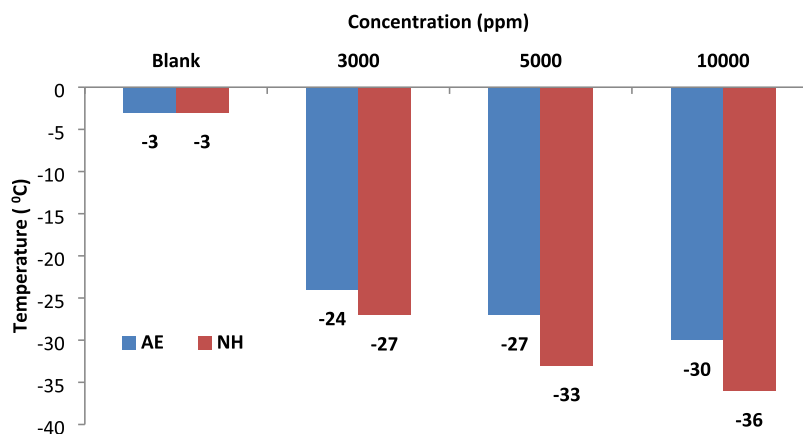

Figure 11. Pour point depressant of the untreated diesel fuel and treated with the prepared copolymer (AE) and with polymer nanohybrid (NH).

Table 2. Detected Pour Point Temperatures at Different Concentrations

sample	blank	3000 ppm	5000 ppm	10,000 ppm
AE	−3	−24	−27	−30
NH	−3	−27	−33	−36

124 cP (pure diesel fuel) to 15.74 cP and 12.8 cP upon adding AE and NH, respectively, at 25 °C. Also, the yield stress value (τ_B) of the diesel fuel was decreased from 576 D/cm^2 (pure diesel fuel) to 541.44 and 477.9 D/cm^2 after treatment with AE and NH, respectively. All these results are in harmony with the previous findings, proving that the NH is more effective

Table 3. Kinematic Viscosity and Viscosity Index of the Untreated Diesel Fuel and Treated with the Prepared Copolymer (AE) and with the Polymer Nanohybrid (NH)

sample	kinematic viscosity, cSt ASTM D-445		viscosity index
	40 °C	100 °C	
blank	3.35	1.308	116 ± 0.1
AE	3.3	1.296	119.13 ± 0.02
NH	3.267	1.288	121 ± 0.01

than AE, where the NH induces a higher decrease of both apparent viscosity and the yield stress than AE. All the results
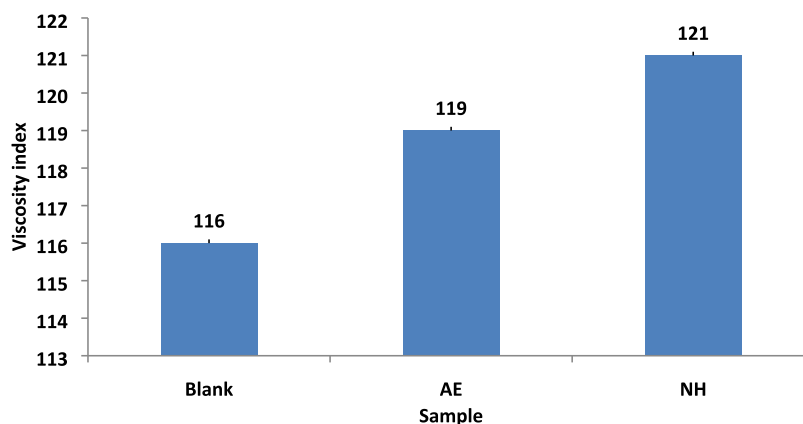

Figure 12. Viscosity Index of the untreated diesel fuel and that treated with the prepared Copolymer (AE) and with the polymer nanohybrid (NH) with an error bar of 0.1 value.
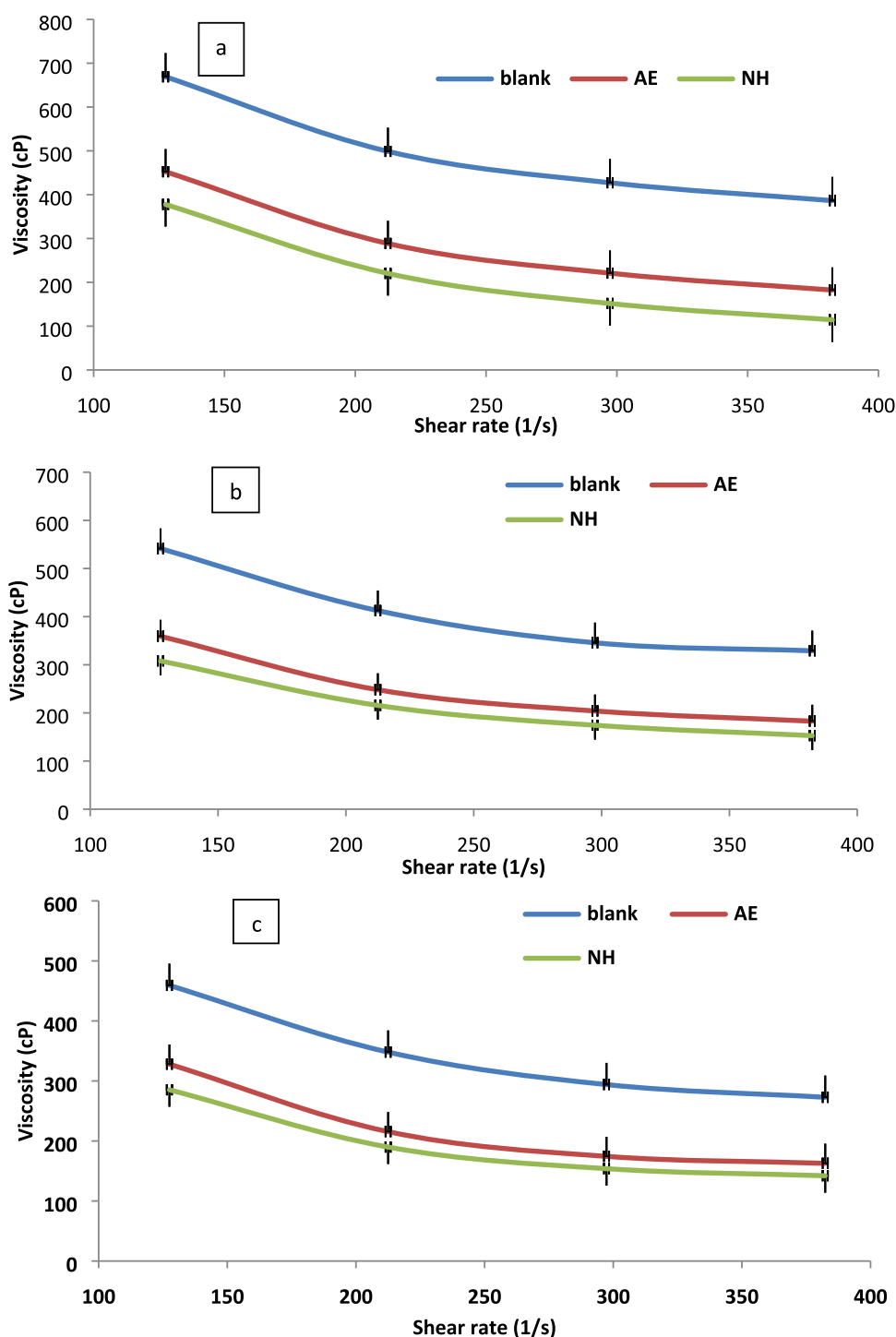
Figure 13. Viscosity–shear rate curve of the untreated diesel fuel and that treated with the prepared copolymer (AE) and with the polymer nanohybrid (NH) at (a) 25 °C, (b) 15 °C, and (c) 0 °C with a standard error bar.

were reproducible after repeating the method more times, indicating that the results were accurate.

3.5. Mechanism of AE and NH as a FI and PPD. The previous literature[44,45] predicts the use of the synthesized polymers as flow improvers; the prepared polymer (AE) should be distributed throughout the wax; this prevents the formation of networks, so that the wax would be separated from each other and still has the small shape that was suspended and stabilized (steric stabilization). NH contains nanosilica and gives the best performance as a pour point

depressant and flow improver for diesel fuel, which could be explained by the presence of the nanosilica throughout the matrix of the polymer improving the thermal stability and the mechanical strength of the copolymer, which are the main reasons for improving the performance.

Also, the phenomenon of the NH having higher compatibility as a flow improver could be explained through two points; first, the NH consists of heteronucleation sites; these lead to more regular and uniform wax crystals that are able to be still dispersed with the tiny shape through the diesel
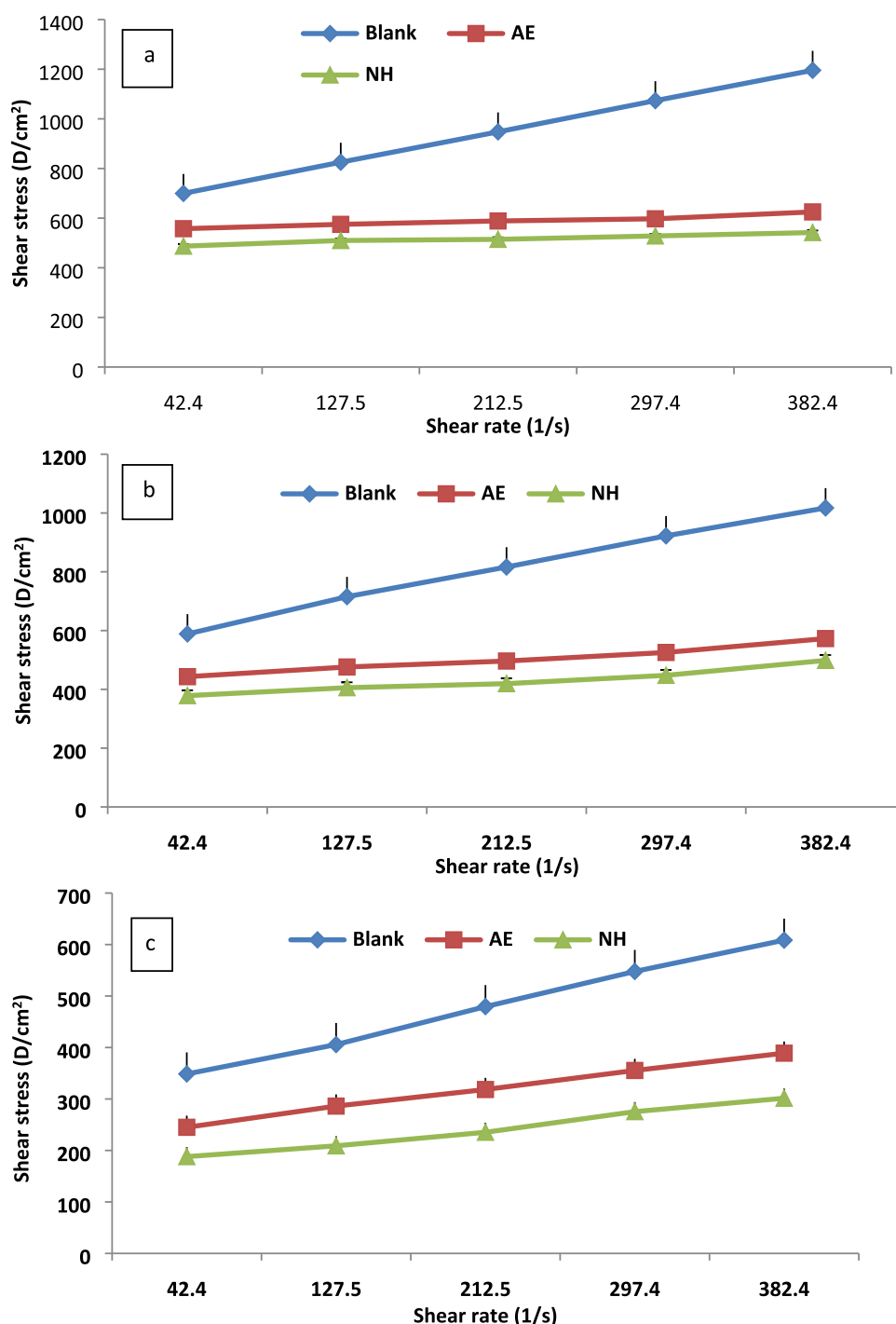
Figure 14. Flow curve of the untreated diesel fuel and that treated with the prepared AE and with NH at (a) 25 °C, (b) 15 °C, and (c) 0 °C with a standard error bar.

fuel, preventing the 3D wax crystal formation,[21] and second, the nanosilica is featured to have high surface energy; this causes the crystallization to occur at a slower rate to maintain a stable energy system.[47] The mechanism is shown in Figure 15.

4. CONCLUSIONS

In the present work, a new copolymer (AE) of the prepared hexadecylmaleamide (HDM) and octyloleate ester (OOE) was prepared by solution polymerization and its nanohybrid was also prepared by emulsion polymerization in the presence of nanosilica. The prepared additives are elucidated by FTIR, [1]H

NMR, DLS, and TEM. The polymer nanohybrid was characterized with high-resolution figures of TEM and DLS to prove their synthesis in the nanoscale. The prepared polymer and its nanohybrid are soluble in diesel fuel and are effective as pour point depressants and cold flow improvers for diesel fuel. The comparative study between our prepared polymer and the nanohybrid samples showed that the polymer nanohybrid (NH) gave the best results as a PPD, FI, and viscosity modifier. From the POM results, it was observed that the wax crystal shape and size were changed from big and tight in the pure diesel fuel to small and separated in that treated

Table 4. Apparent Viscosity (η_{app}) and Yield Stress Values (τ_B) of Pure Diesel Fuel and That Treated with 10,000 ppm AE and NH at 0, 15, and 25 °C

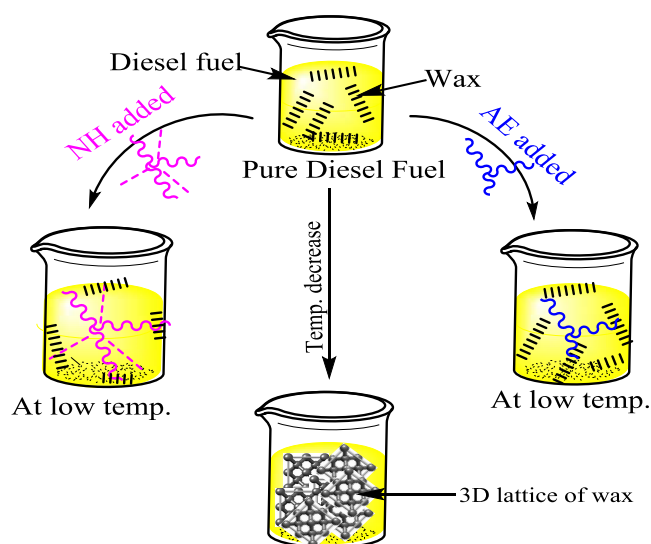| sample	temp (°C)	apparent viscosity (cP)	yield stress, (D/cm^2)
blank	0	66.18 ± 0.01	279.44 ± 0.01
	15	106.43 ± 0.01	492.64 ± 0.01
	25	124 ± 0.01	576 ± 0.01
AE	0	35.721 ± 0.01	211.64 ± 0.01
	15	30.87 ± 0.02	410.2 ± 0.02
	25	15.74 ± 0.03	541.44 ± 0.03
NH	0	29.34 ± 0.02	153.82 ± 0.02
	15	28.18 ± 0.05	345.44 ± 0.05
	25	12.8 ± 0.04	477.9 ± 0.4

Figure 15. Predicted mechanism of the prepared AE and NH as a flow improver and pour point depressant of diesel fuel.

with AE and NH by the repulsion of the polar groups, leading to a decrease in the viscosity of the diesel fuel. Therefore, the newly prepared copolymer (AE) and its nanohybrid (NH) could be used as a novel flow improver and pour point depressant for the diesel fuel, especially the nanohybrid that gave the best results. Also, the nanoparticles affect the efficiency of the prepared compound, so different nanoparticles could be used and tested for their effect as a PPD, FI, and viscosity modifier.

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