Influence of Copolymer Based on Oleic Acid and Its Nanohybrid as Cold Flow Improvers for 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 FT-IR, ^{1}H-NMR,DLS, and 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.

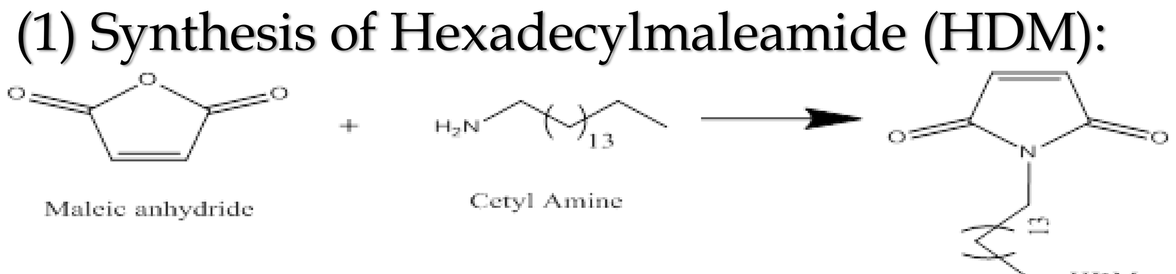
Introduction

Diesel-fuel plays a crucial part in providing the demand in energy and is mostly used in a variety of commercial and industrial sectors as well as in the agriculture, our life-day, and other social spheres[1].Wax crystals readily develop network architectures in diesel as the temperature decreases[2], and the intense stacking of these crystals causes them to clog filters and negatively impact diesel flow ability. Diesel crystallization creates challenges for storage, disposal, and transportation, as well as billions of dollars in annual economic losses globally. Therefore, because to its poor cold flow qualities, diesel's use and popularity are restricted. Utilizing polymeric additives is a cost-effective and environmentally friendly technique among the several methods (thermal process, mechanical methods, and also polymeric-additives) that used for improving the cold-flow of diesel.

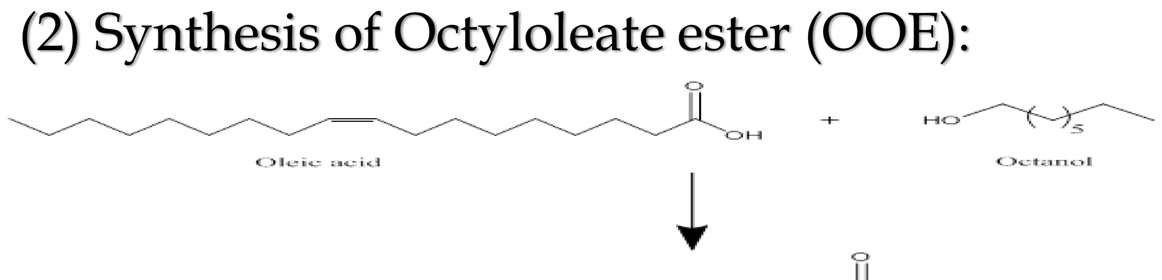
Methodology

❖ Synthesis of Copolymer (AE):

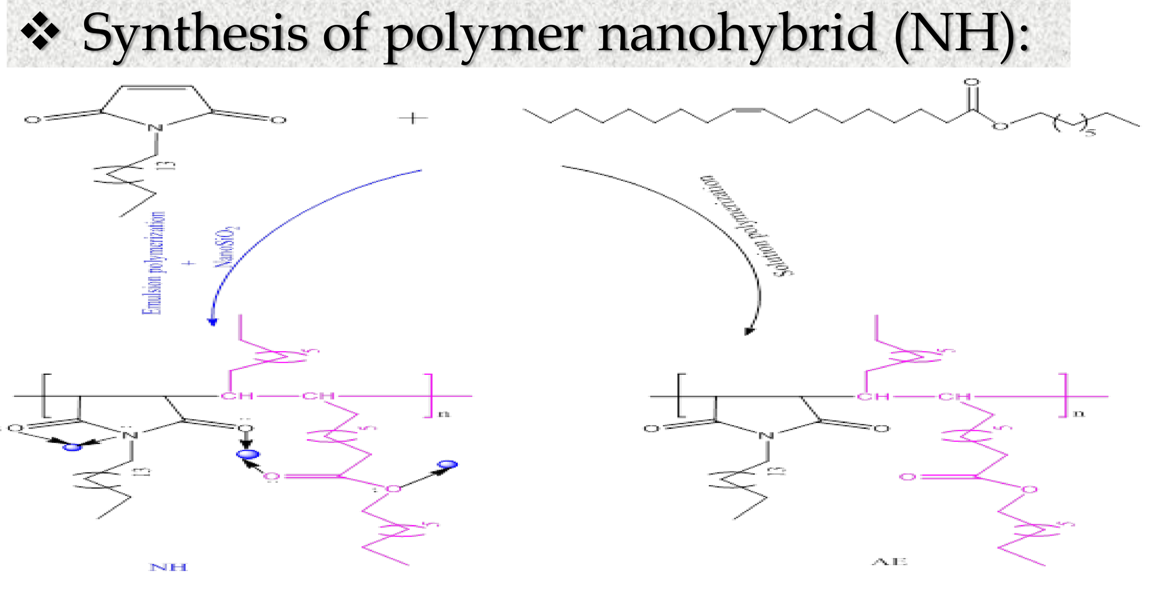
(1) Synthesis of Hexadecylmaleamide (HDM):



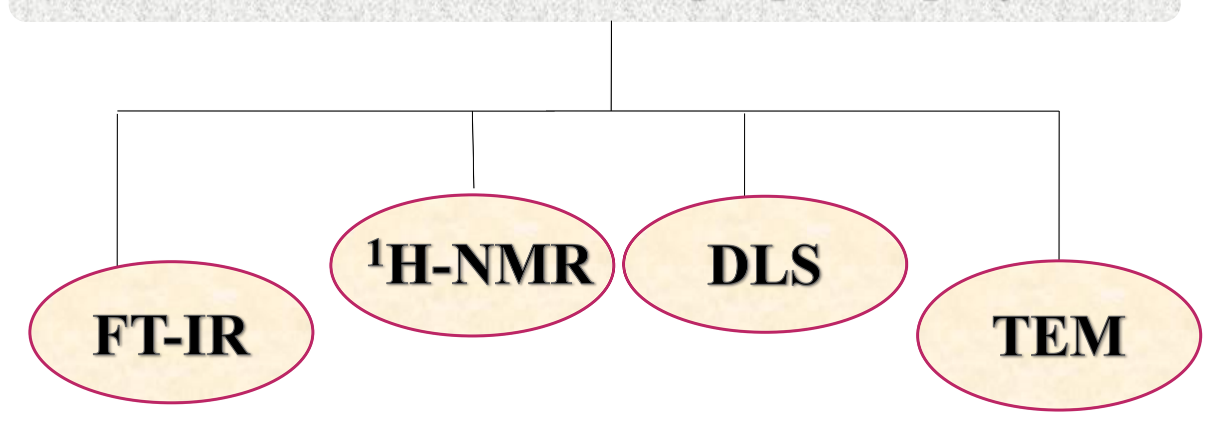
(2) Synthesis of Octyloleate ester (OOE):



❖ Synthesis of polymer nanohybrid (NH):



(2) Characterizations of the prepared polymers.



(3) Evaluation of the polymers

A) As Pour-Point Depressant (DPD).

B) As Viscosity Index Improver (VII).

C) Study The Rheological Behavior.

Results and Discussion

(1) Characterizations of the prepared polymers:

❖ **FT-IR Analysis:**

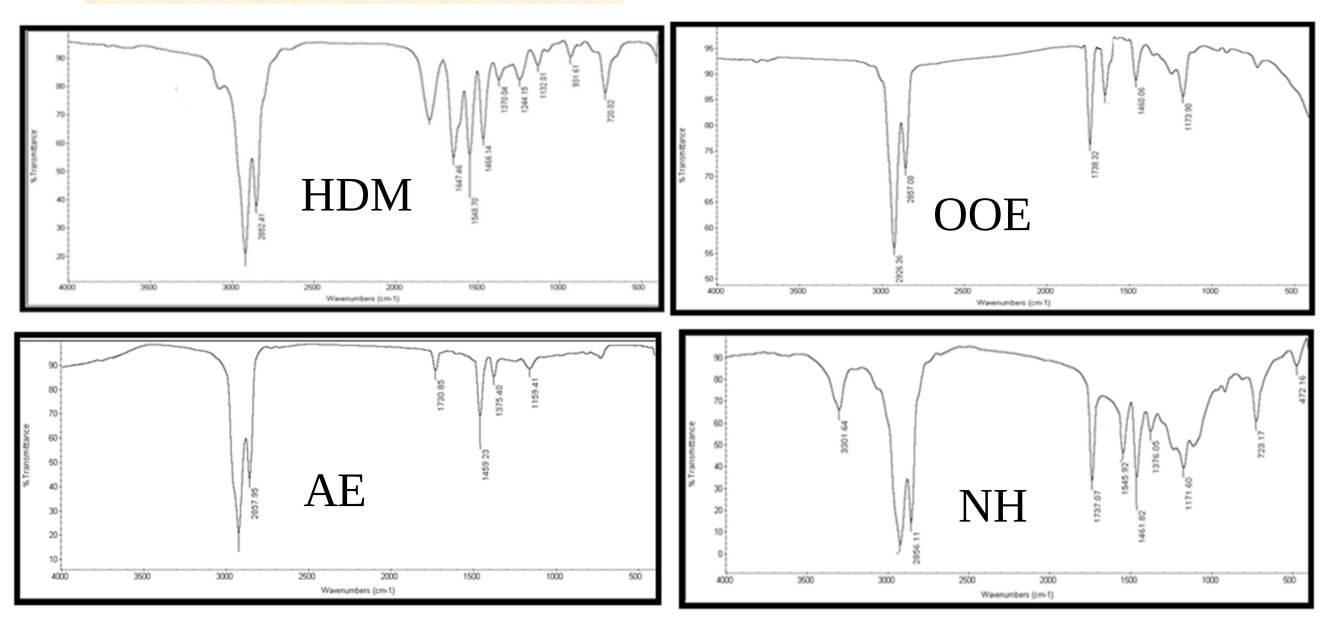


Fig.(1): FT-IR spectra of prepared polymers HDM,OOE,AE and NH.

❖ **^{1}H-NMR Analysis:**

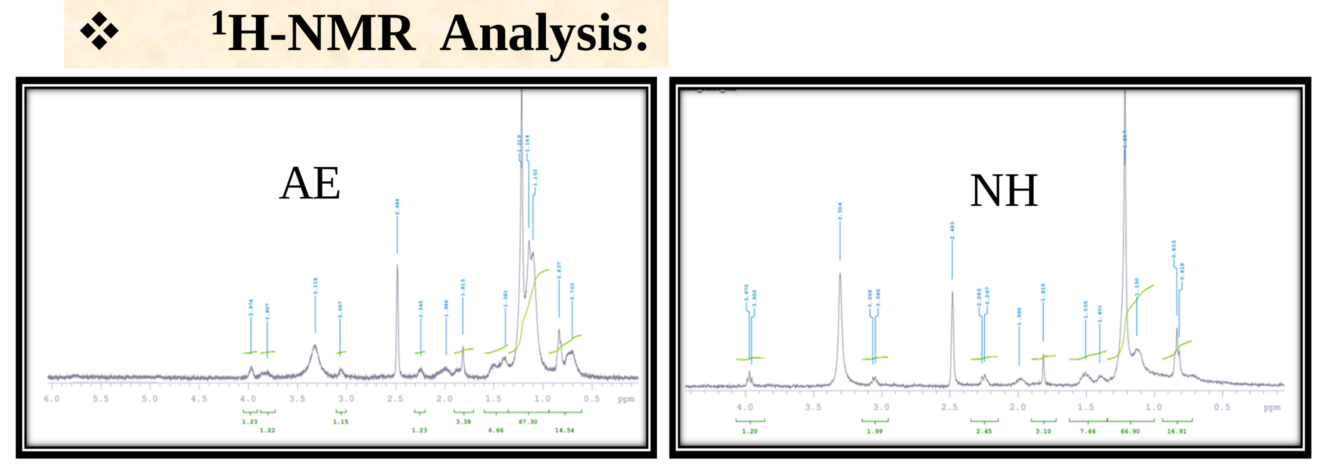


Fig.(2): ^{1}H-NMR spectra of prepared polymers AE and NH.

❖ **DLS image:**

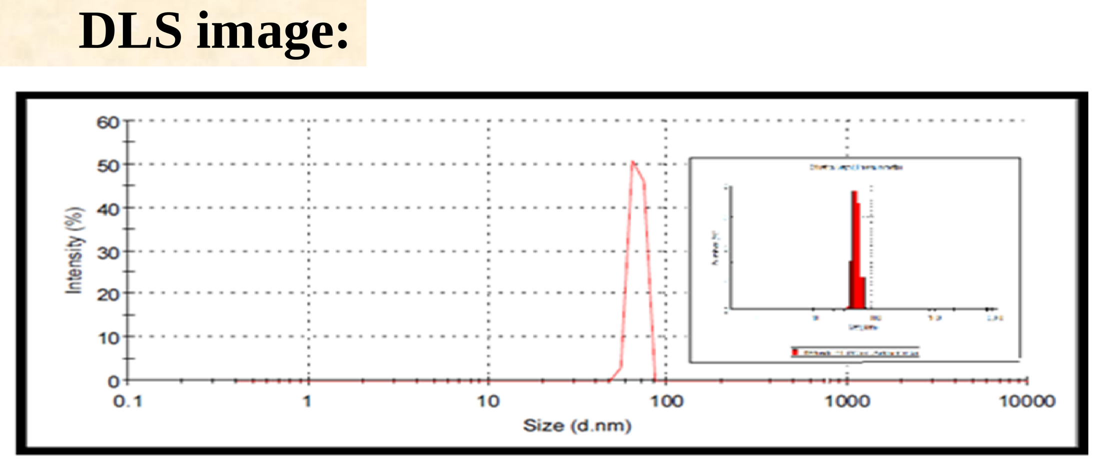


Fig.(3): DLS image of polymer nanohybrid (NH)

❖ **HR-TEM image :**

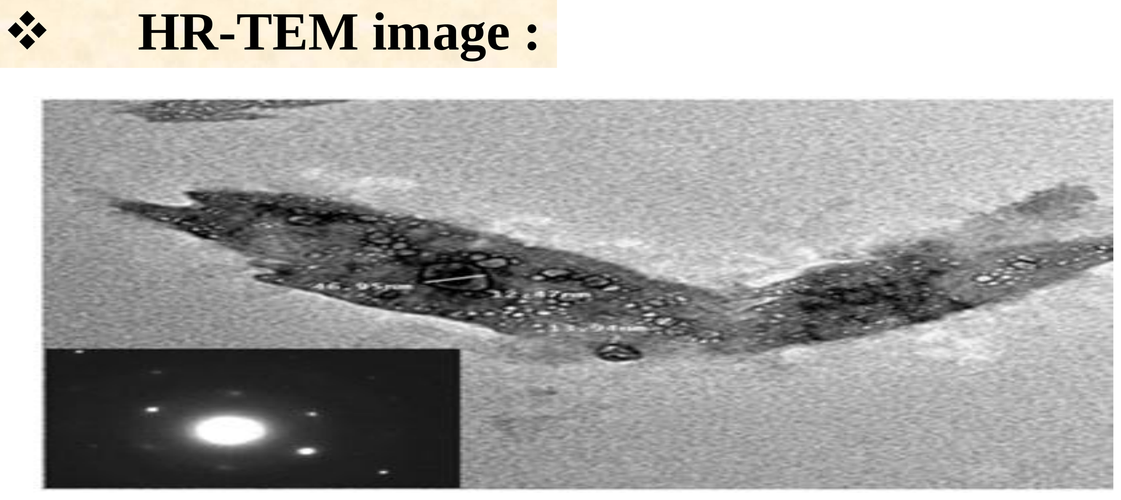


Fig.(4): HR-TEM analysis image of polymer nanohybrid (NH)

(2) Evaluation of the polymers:

➢ The wax crystal morphology

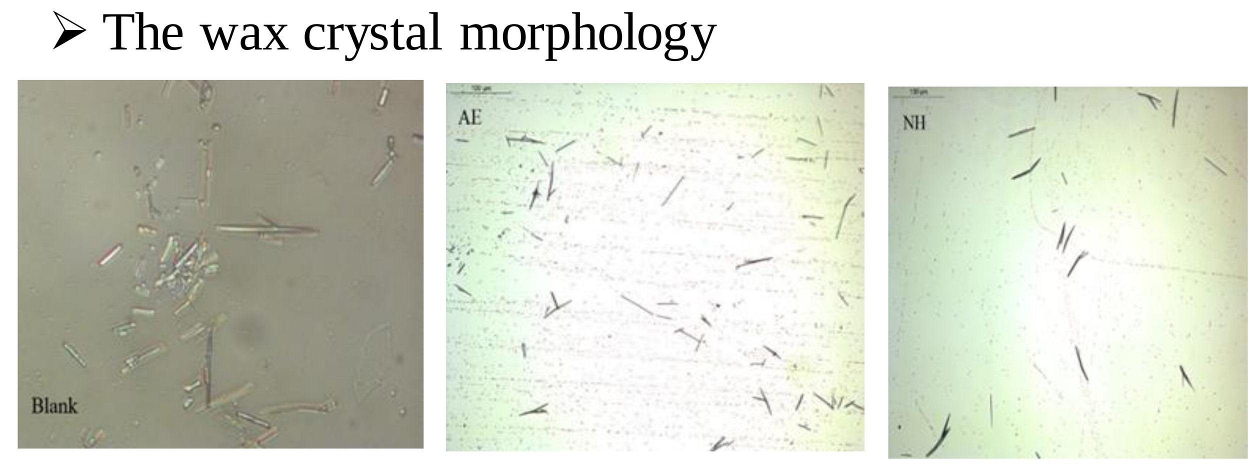


Fig.(5): The polarized optical microscope image of the wax of diesel-fuel samples [Blank, with prepared Copolymer (AE) and with polymer nanohybrid (NH)]

A) AS Pour point Depressant (PPD)

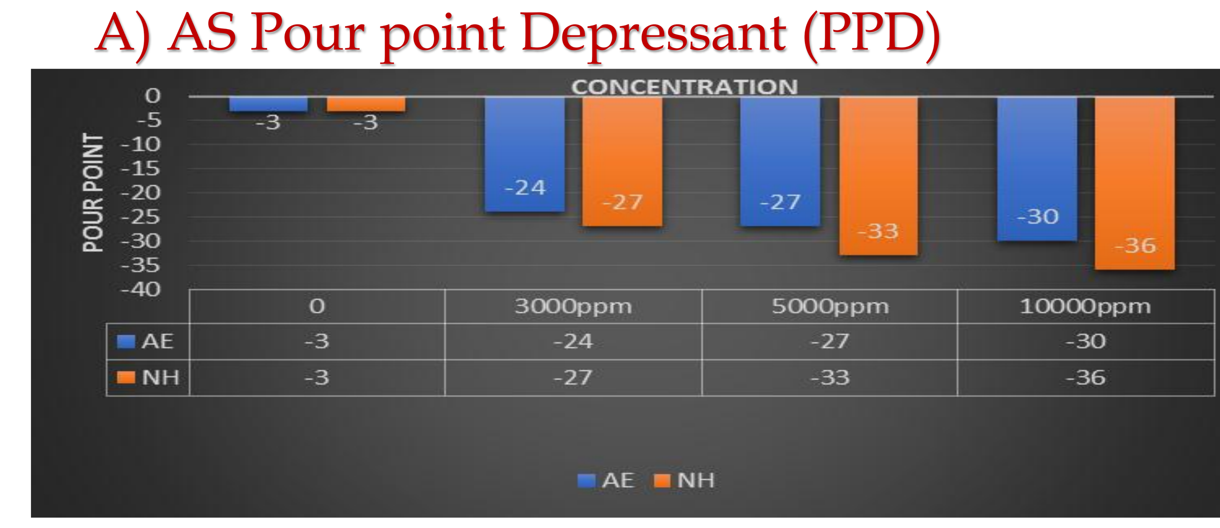


Fig.(6): PPT of the untreated diesel fuel and treated with prepared Copolymer (AE) and with polymer nanohybrid (NH)

B) AS Viscosity Index Improver (VII)

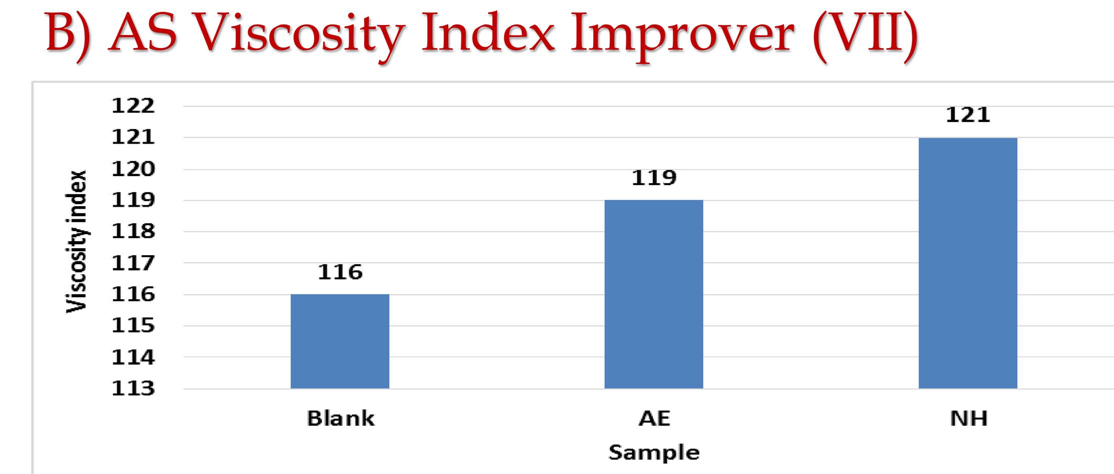


Fig.(7): VI of the untreated diesel-fuel and that treated with prepared Copolymer (AE) and with polymer nanohybrid (NH)

Table (1): Kin. V and VI of the untreated diesel fuel and treated with prepared Copolymer (AE) and with polymer nanohybrid (NH)

Sample	Kinematic viscosity, cSt ASTM D-445		Viscosity index (VI)
	40 °C	100 °C	
Blank	3.35	1.308	116
AE	3.3	1.296	119.13
NH	3.267	1.288	121

C) Study The Rheological Behavior

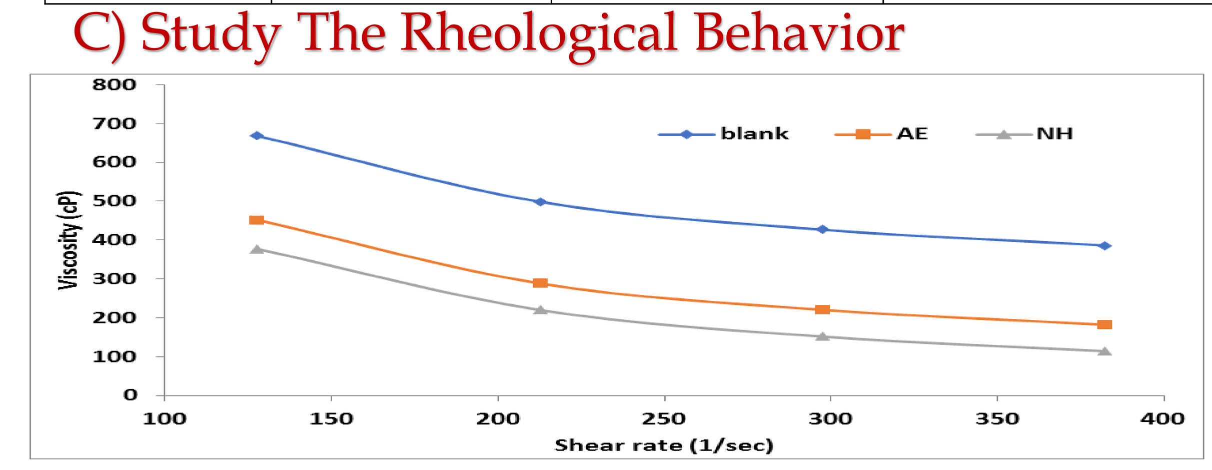


Fig.(8) : The Viscosity–Shear Rate Curve of the untreated diesel fuel and treated with prepared Copolymer (AE) and with polymer nanohybrid (NH) at the 25 °C.

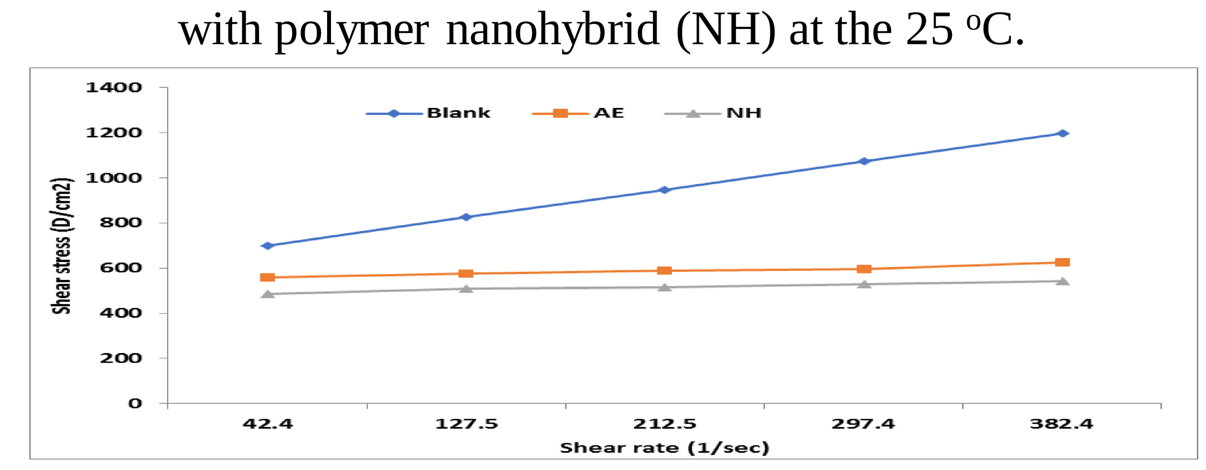


Fig. (9): The Flow Curve of the untreated diesel fuel and treated with prepared Copolymer (AE) and with polymer nanohybrid (NH) at the 25 °C

Table (2): The apparent-viscosity (ηapp) and yield-stress values (τB) of pure diesel-fuel and that treated by 10,000 ppm from AE and NH at room temperature.

Sample	Apparent Viscosity, cP	Yield Stress, D/Cm^2
Blank	124	576
AE	15.74	541.44
NH	12.8	477.9

Conclusions

1) Synthesis of copolymer (AE) and nanohybrid(NH) and they were elucidated by FT-IR , ^{1}H-NMR, DLS and TEM.
2) The prepared polymer and its nanohybrid are soluble in diesel fuel and are effective as PPDs and cold flow improver for diesel fuel.
3) The comparative study between our prepared polymer and the nanohybrid samples showed that the polymer nanohybrid (NH) gave the best results as PPD, FI and viscosity modifier.

References:

(1) Yang, T.; Wu, J.; Yuan, M.; Li, X.; Yin, S.; Su, B.; Yan, J.; Lin, H.; Xue, Y.; Han, S. Influence of Polar Groups on the Depressive Effects of Polymethacrylate Polymers as Cold Flow Improvers for Diesel Fuel. Fuel 2021, 290, 120035.
(2) Li, X.; Yuan, M.; Xue, Y.; Lin, H.; Han, S. Tetradecyl Methacrylate-N-Methylolacrylamide Copolymer: A Low Concentration and High-Efficiency Pour Point Depressant for Diesel. Colloids Surfaces A Physicochem. Eng. Asp. 2022, 642, 128672.