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The Performance of Polymethyl Methacrylate/Clay Nanocomposite as Novel Pour Point Depressant on Rheological Properties of Model Waxy Crude Oil

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Abstract
A novel polymeric nanocomposite pour point depressant (PPD), based on polymethyl methacrylate (PMMA) and montmorillonite (MMT) clay, was synthesized and characterized. For a comprehensive comparison, the influence of neat polymethyl methacrylate (PMMA) and PMMA/clay nanocomposite on reducing pour point, gelation point, apparent viscosity, and yield stress of a model waxy crude oil was investigated, followed by evaluation of their performances precisely. The rheometry test results showed that the addition of 400 ppm of PPMA and 800 ppm of PMMA/clay nanocomposite to waxy crude oil reduced the pour point from 13˚C (for untreated sample) to 0 and -3 ˚C, respectively. Thus, the addition of PMMA/clay nanocomposite to waxy crude oil resulted in a 120% reduction in the pour point.

Key words: Pour point depressant, Polymeric nanocomposite, Montmorillonite, Model waxy crude oil, Rheological properties.

Introduction
Some crude oil samples are very difficult to transport through the pipelines in the cold sessions and climates due to their high wax content [1]. The formation of waxy crystals at low temperatures leads to reduce crude oil flowability, and it could dramatically interrupt the transportation process [2]. The waxes mainly consist of long-chain paraffin with a few amounts of branched-chain paraffin, cycloparaffins, and aromatics [3]. The wax precipitation process is defined by some characteristics, including wax appearance temperature (WAT), gelation, and pour points, representing particular states of waxy crude oil during the cooling. At the WAT, the first waxy crystals appear, and by further cooling, more waxy crystals form [4]. They have more interaction with each other, and the waxy aggregates appear rapidly. The aggregates join together to form a strong waxy network, leading to the emergence of a gel structure at the gelation point. The waxy crude oil reaches its pour point and behaves like a solid by continued cooling [5]. The formation of the solid phase begins with the crystallization process of waxes which consists of three mechanisms of nucleation, growth, and aggregation [6]. There are many strategies to deal with the crystal formation at the temperatures below the WAT, like the pipeline thermal heating or insulation [7], mechanical pigging [8], chemical inhibition [9-12], and biological [13] methods. The utilization of chemical inhibitors such as pour point dispersant (PPD) enhances the flowability of waxy crude oil at low temperatures. These chemical additives alter waxy crystals morphology and prevent them from forming a strong waxy 3D network. However, a chemical inhibitor that could be efficient for all the crude oil samples has never been found [14,15].
A new generation of the PPDs that is based on nanotechnology, including nanocomposites, attracts much attention in recent years. Nano-silica and modified montmorillonite nanoclay have been very populated in recent studies [16,17]. Wang et al. have investigated the impact of nano-hybrid and ethyl-vinyl-acetate on the pour point and apparent viscosity of a waxy crude oil sample. They concluded that the nano-hybrid inhibitor was more efficient than ethyl-vinyl-acetate [18]. Yang et al. synthesized a nono-hybrid inhibitor by hydrophilic nano-silica and poly octadecyl acrylate and compared its performance for wax inhibition with poly octadecyl acrylate[19]. It was revealed that the utilization of the nano-silica increased the inhibitor efficiency to reduce the gelation point and yield stress of the sample. In another study, a nanocomposite poly octadecyl acrylate

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and modified nanoclay was synthesized using a toluene solvent blending procedure. The modified nanoclay acted as a base and absorbed the polymer on its structure, and thereby, a nanocomposite is formed. The results showed that the synthesized polymeric nanocomposite PPD had a better performance to reduce the gelation point, apparent viscosity, and yield stress compared to the neat poly octadecyl acrylate. The microscopic images have demonstrated that the polymeric nanocomposite PPD increased the size of the waxy aggregates and reduced their interactions [20]. The effect of copolymer ethyl-vinyl-acetate/nano-MMT on the pour point of a crude oil sample with 25wt.% wax content was assessed by Li et al. It was found that vinyl-acetate had a significant impact on the performance of the inhibitor and reported the reduction of pour point from 34 to 2˚C due to the addition of 0.08 wt.% EVA/nano-MMT [21].

In this study, polymethyl methacrylate/clay nanocomposites (PMMA/clay nanocomposites) were synthetized by dimethylformamide solvent blending. In addition, the influences of the neat PMMA and the PMMA/clay nanocomposite on the rheological properties of the model waxy crude oil like pour point, yield stress, viscosity, and dynamic viscoelastic modules were investigated using standard rheological tests. Moreover, the microscopic observations helped us study the morphology and shape of the waxy crystals in the presence of the above-mentioned inhibitor.

Materials and Methods

The polymethyl methacrylate (PMMA-830-IH) was provided by the Korean LG Company with a molecular weight of 149000 Da. The original nanoclay and modified nanoclay (Cloisite 20A) were purchased from American Sigma-Aldrich and Southern Clay companies. The purchased nanoclay was modified by dimethyl, dehydrogenated tallow, and quaternary ammonium through the cationic exchange. The dimethylformamide (DMF), acetone, toluene, n-heptane, n-pentane, petroleum ether were provided from Merck Chem. Co. All the tests were performed using a model waxy crude oil with 20 wt.% wax content. It was prepared by adding an adequate amount of raffinate to Isfahan Refinery crude oil. The physical properties of Isfahan refinery waxy crude oil and raffinate are tabulated in Table 1.

Montmorillonite (MMT) was used as a base for PMMA, which leads to its better dispersion in the organic phase. Montmorillonite nano-clay is a layered silicate mineral with a 2:1 type layer structure, i.e. it has two tetrahedral sheets sandwiching a central octahedral sheet [16]. Due to isomorphs substitution, the nano-clay is negatively charged, and some hydrated Na+ or K+ species exist in the interlayer to balance the negative charge [22]. To increase the stability of the suspension, quaternary ammonium salt surfactants are often used to modify nano-clay such that organic cations replace the interlayer hydrated Na^+ or K^+, i.e. cation exchange, enlarging layer spacing and enhancing lipophilicity of the nano-clay. The organically modified nano-clay is easier to disperse in a polymer matrix and is more compatible with the organic phase [23]; therefore, a stable suspension in the organic phase could be reached.

Table 1 Physical properties of Isfahan refinery waxy crude oil and raffinate.

	Physical property	Value
Waxy Crude Oil	Density at 15˚C (gr/m^3)	0.8958
	Viscosity at 45˚C (mm^2/s)	0.5253
	Wax content (wt.%)	5.68
	Asphaltene content (wt.%)	0.6
Raffinate	Density at 15˚C (gr/m^3)	0.8891
	Pour point (˚C)	35
	Viscosity at 60˚C (mm^2/s)	37.71
	Viscosity at 100˚C (mm^2/s)	10.98
	Paraffin (wt.%)	60.8
	Naphthenic (wt.%)	37
	Aromatic (wt.%)	2.2

PMMA/Clay Nanocomposite Synthesis

The PMMA/clay nanocomposite was prepared by solvent blending protocol. At First, PMMA was placed in an oven at 80 ˚C, and then it was dissolved in DMF solvent with 0.1 g/ml concentration, and 0.1 g/ml Montmorillonite nanoclay was dispersed in PMMA/DMF solution completely under Ultrasonic Homogenizer. Finally, the obtained suspension was heated up to 70 ˚C, the solvent was evaporated, and PMMA/clay nanocomposite powder remained.

In order to have a simple and realistic comparison of the performances of the PMMA versus PMMA/clay nanocomposite, the PMMA to nanoclay mass ratio was considered identical at 1:1 [19]. Also it must be noted that, modified nanoclay does not alter the rheological properties of waxy crude oil, because it is not capble of affecting the waxy crystal formation or deposition itself [20].

Measurement Methods

The physicochemical properties of the PPDs were estimated using an XRD instrument (D8 ADVANCED, Burker, Germany) and an FT-IR instrument (6300, Japan). The pour point was determined in accordance with ASTM D97 in which all the samples were cooled from 30 °C to their pour points, and for every 3˚C, the flowability of the sample is observed. To increase the pour point values accuracy, the tests were repeated three times, and the average of these runs was considered as the pour point of the sample. During the cooling process, the pour point is the lowest temperature at which the sample does not flow anymore [24]. The rheological shear rotational tests were conducted to determine the flow curve and apparent viscosity of the waxy crude oil by a rheometer (MCR 301, Anton Paar, Austria) equipped with a Peltier heating system and cone and plate geometry of 25 mm size with an angle of 2°. In each test, the sample was initially cooled from 50 to 5˚C with the cooling rate of 2˚C/min to impose a specific thermal history, and then the rotational shear tests were conducted with the shear rate increasing in the range of 5 to 200 s^{-1} gradually. Some oscillatory shear tests were also performed to determine the storage G' and loss G" modules of the samples. The tests were conducted at an adequately low frequency of about 1 Hz and the cooling rate of 1˚C/min at the temperature range of 40 to 10˚C. Since the crystal network must not be destroyed, a low shear strain value of about 0.0001 was chosen for all the tests [20,25]. Moreover, a polarized light microscope (Olympus Bx41, Japan) was implemented to study the effect of PPDs on the shape and size of the waxy crystals and the emerging waxy aggregates.

Results and discussion

Physico-Chemical Characteristics

The XRD analysis was utilized in the range of 2θ (1 to 16), to assess the crystal structure of the nanoclay in the form of original, modified, and compounded into the polymer matrix, and the patterns are illustrated in Fig. 1(a). The interlayer spaces of the original nanoclay, modified nanoclay, and PMMA/clay nanocomposite are determined by Bragg`s law and are tabulated in Table 2.

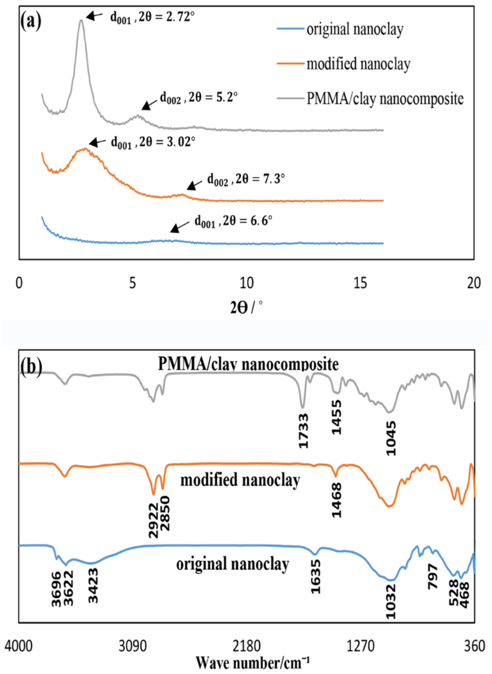


Fig. 1 XRD patterns (a) and FT-IR spectra (b) of the original nanoclay, modified nanoclay, and PMMA/clay nanocomposite.

Table 2 Interlayer spacing of the original nanoclay, modified nanoclay, and PMMA/clay nanocomposite.

Inhibitor	d_{001} (nm)	d_{002} (nm)
Original nanoclay	1.338	-
Modified nanoclay	2.923	1.210
PMMA/clay nanocomposite	3.245	1.698

PPD Effect on Pour Point

In Fig. 2, the percent of pour point reduction due to the utilization of each inhibitor at different concentrations is shown.

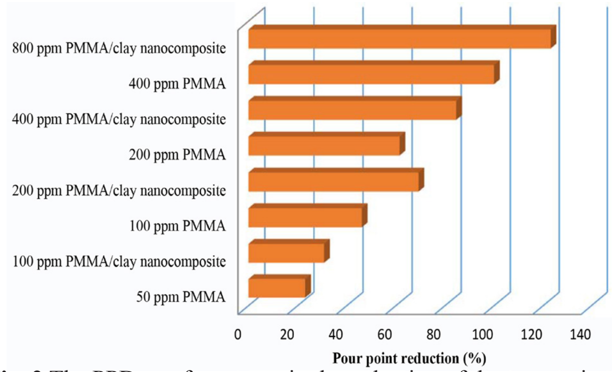


Fig. 2 The PPDs performances in the reduction of the pour point.

Higher pour point reduction is achieved with the PMMA/clay nanocomposite, and the efficiency is increased by increasing the PPD concentration. The pour point of the untreated waxy crude oil is measured to be 13˚C; however, the additions of 50 ppm of the PMMA and 100 ppm of the PMMA/clay nanocomposite reduce the pour point to 10˚C and 9˚C, respectively. The presence of 100, 200, 400 ppm of the PMMA causes the pour point decrease to 7, 5, 0 ˚C, while for 200, 400, and 800 ppm of the PMMA/clay nanocomposite, the pour point values are 4, 2, -3, respectively. Better performance of the PMMA/clay nanocomposite is observed in comparison with the PMMA in the reduction of the pour point.

PPD Effect on Viscoelastic Properties of Waxy Crude Oil

The changes of the dynamic modules as a function of temperature were determined by conducting the oscillatory shear tests for the untreated and treated waxy crude oil at different wax contents. The G' module is a measure of the ability of the material to store energy within its structure and indicates the elastic behavior of the material, while the G" module is a measure of energy which is lost often as the heat and expresses the viscous behavior of the material [26]. As it is shown in Fig. 3, the trends of the graphs are similar. When the oil sample is cooled, both of the modules are flat and constant at the high temperatures, follow with a sharp increase by a further reduction in the temperature and beyond that, the modules raise at slower rates. At the high temperatures, the viscous module (G") dominants, while by reducing the temperature, the elastic module (G') increases faster, the modules pass through an intersection, and G' remains above the G" curve. The trends of the dynamic modules during the cooling demonstrate the emerging of a strong waxy gel network with elastic properties within the crude oil medium. During cooling, the solid-like behavior of waxy crude oil dominates its liquid-like behavior at the gelation point [27].

The shear oscillatory test results are used to determine the gelation point of the treated and untreated waxy crude oil. Indeed, the gelation point is a temperature at which the waxy crystals join together and forms a 3D waxy network in the fluid medium [28]. The treatment of the waxy crude oil with the PMMA and PMMA/clay nanocomposite leads to a decrease in the gelation point significantly. The additions of 100, 200, 400 ppm of the PMMA make the gelation point decrease to 21.3, 20.1, 18.2 ˚C, respectively. In contrast, the utilization of 200, 400, and 800 ppm of the PMMA/clay nanocomposite results in the gelation points are reduced to 20.3, 17.2, 16.2 ˚C, respectively.

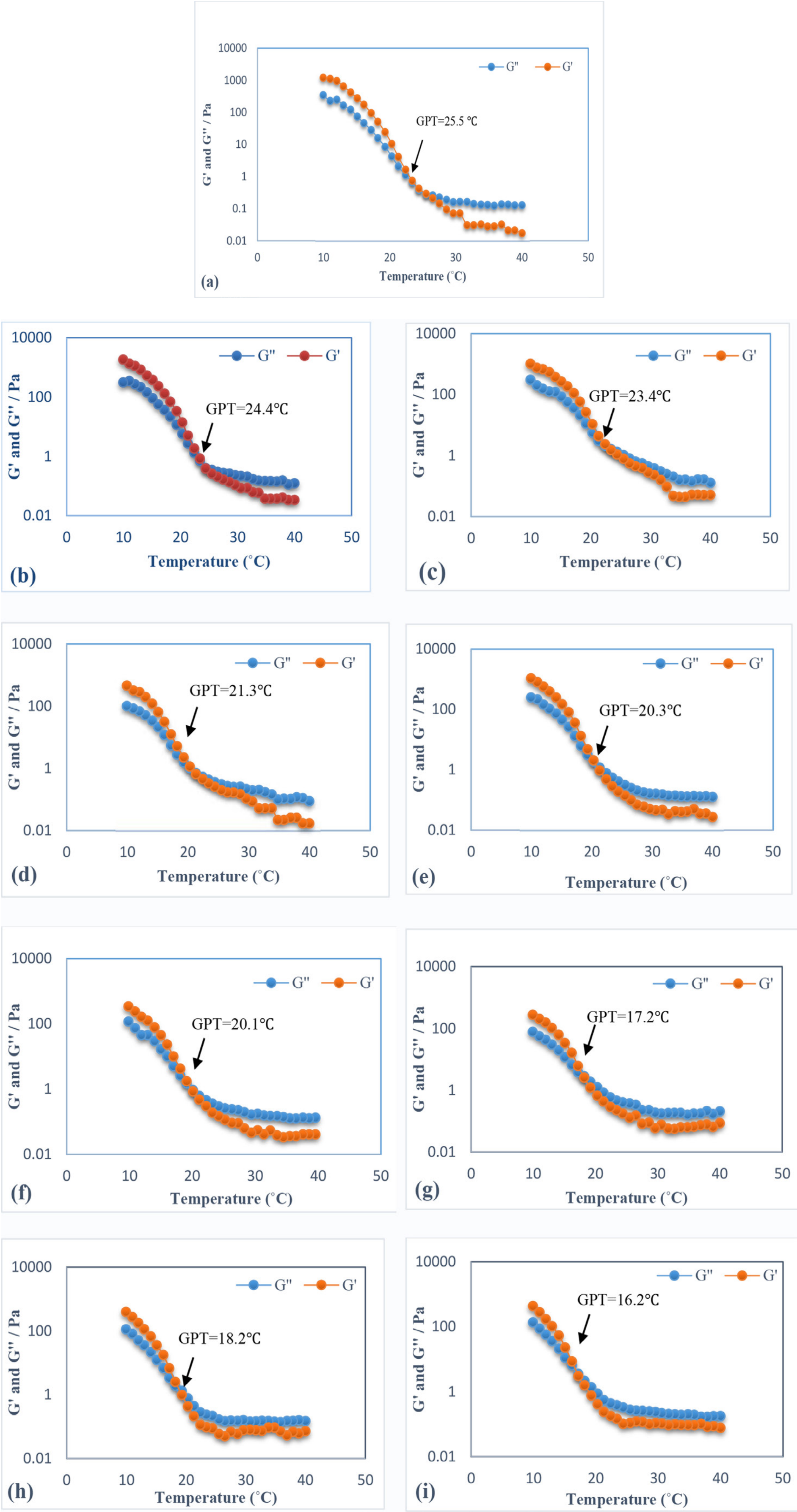


Fig. 3 Rheological dynamic modules of the waxy crude oil in cooling phase: a) Untreated crude oil; b) Treated with 50, d) 100, f) 200, and h) 400 ppm of PMMA; Treated with c) 100, e) 200, g) 400 and i) 800 ppm of PMMA/clay nanocomposite.

It is noticeable that the PMMA/clay nanocomposite is more influential in the reduction of the gelation point of the waxy crude oil than the neat PMMA. An unexpected trend is observed in G' and G" values for treated samples. For example, the G' for Fig. 3 e is higher than Fig.3 d, while the expectation is the reduction in G' for higher PPD dosage due to a further decrease in waxy structure strength. This uncommon trend may be due to the experimental error because the differences between the G' and G" values are very small (in a narrow interval) for the different samples in this study. Moreover, nanoclay in low temperatures may show another behavior, which results in such an unusual phenomenon that has to be more investigated by further analyzes.

PPDs Effect on Time Independent Rheological Properties of Waxy Crude Oil

Yield Stress

In Fig. 4, the flow curves of the treated and untreated waxy crude oil samples for the shear rate ranging from 10^{-1} to 200 s^{-1} at 5 °C are shown. By increasing the shear rate, shear stress increases. The presence of the PPDs leads to a decrease in the shear stress since the waxy crystal network within the fluid medium is weakened. The yield stresses of the samples are determined by fitting the experimentally obtained flow curves with the rheological Bingham-plastic model, which is defined as [29]:

$$\dot{\gamma} = 0 \qquad \tau \leq \tau_0^B$$

$$\tau = \tau_0^B + \mu_B \dot{\gamma} \qquad \tau \geq \tau_0^B$$

where τ, $\dot{\gamma}$, τ_0^B and μ_B are shear stress, shear rate, Bingham yield stress, and Bingham viscosity, respectively. The Bingham yield stress and Bingham viscosity values are determined with good correlation coefficients and tabulated in Table 3.

Table 3 Rheological Bingham plastic model fitting results.

Sample Condition	τ_0^B (Pa)	μ_B (Pa·S)	R^2
Waxy crude oil	73.5	0.308	0.9824
50 ppm PMMA	68.3	0.2755	0.9776
100 ppm PMMA/clay nanocomposite	47.4	0.1914	0.9975
100 ppm PMMA	52.5	0.2877	0.9943
200 ppm PMMA/clay nanocomposite	39.4	0.1424	0.959
200 ppm PMMA	33.4	0.1319	0.9894
400 ppm PMMA/clay nanocomposite	21.8	0.1426	0.9972
400 ppm PMMA	25.3	0.1522	0.9988
800 ppm PMMA/clay nanocomposite	13.8	0.1483	0.9959

There are clear trends of decrease in the Bingham yield stress and viscosity of the waxy crude oil which is treated by the PMMA/clay nanocomposite. As shown in Fig. 4, by treating the waxy crude oil samples with PPDs, the shear stress decreases due to the formation of a weaker waxy network. The utilizations of 100, 200, 400 ppm of the PMMA make the yield stress reduce from 74.485 Pa (for untreated sample) to 52.498, 33.413, 25.293 Pa, respectively, while for 200, 400, and 800 ppm of the PMMA/clay nanocomposite, the yield stress reduces to 39.390, 21.845 and 13.846 Pa respectively. The results confirm a better performance of the PMMA/clay nanocomposite than the PMMA in reducing the yield stress.

Apparent Viscosity

In this investigation, the rheological flow curves of the treated and untreated waxy crude oil were obtained by conducting the rotational shear tests (Fig. 4). Another time-independent rheological property of the samples, the apparent viscosity could be obtained from their flow curves. Fig. 5 shows an increase in the PMMA and PMMA/clay nanocomposite contents decreases the apparent viscosity of the waxy crude oil. The apparent viscosity values for the treated and untreated waxy crude oil samples are determined at a shear rate of 148 s^{-1} and reported in Table 4. The presence of 100, 200, 400 ppm of the PMMA reduces the apparent viscosity to about 25.71, 60.95, and 63.76%, respectively, while for 200, 400, and 800 ppm of the PMMA/clay nanocomposite, its values achieve to 63.11%, 67.99%, 75.56% reduction, respectively. The PMMA/clay nanocomposite has more impact on the apparent viscosity than the same amount of the neat PMMA.

Microscopic Observations

The impacts of the PMMA and PMMA/clay nanocomposite on the size, dispersity, and the morphology of waxy crystals in the crude oil at 0 ˚C are investigated visually through microscopic images shown in Fig. 6. Many tiny waxy crystals with a completely irregular dispersion pattern are observed in the image of an untreated waxy crude oil sample (Fig. 6(a)). The addition of 400 ppm of the PMMA leads to form small waxy crystal aggregates, and thereby, the contact area between the solid particles is reduced, which is shown in Fig. 6(b). In accordance with expectations, the utilization of the modified nanoclay in the form of the PMMA/clay nanocomposite has an advantage compared to the neat PMMA, which is clearly proved in Fig. 6(c). After the addition of 800 ppm of the PMMA/clay nanocomposite with equal concentrations of the PMMA and nanoclay, the waxy aggregates become larger with more regular and compact shapes.

A descriptive explanation of PMMA/clay nanocomposite mechanism

The description of the performance mechanisms of the PPDs is schematically presented in Fig. 7.

The polymeric PPDs consist of two nonpolar (red side alkyl branches) and polar (green polymeric main chains) parts. The nonpolar part is corresponding to adsorb the waxy crystals on its surface, and the polar part decreases the crystal/crystal and crystal/oil interactions, and thereby the size of the waxy aggregates is increased, and they are inhibited from forming the waxy network. The modified nanoclay provides many adsorption sites for the polymer macromolecules to settle on, leading to the formation of the polymeric nanocomposite PPD. The modified nanoclay arranges the polymers on its structure in a regular pattern, which results in more compact, abundant, and regular in shape waxy aggregates at the low temperatures.

Table 4 Summarized rheological properties of the treated/untreated waxy crude oil.

Sample Condition	Pour Point (˚C)	Gelation Point (˚C)	Apparent Viscosity at 5 ˚C and 148 s^{-1} (Pa.s)
Waxy crude oil	13	25.5	1.006
50 ppm PMMA	10	24.4	0.785
100 ppm PMMA/clay nanocomposite	9	23.4	0.526
100 ppm PMMA	7	21.3	0.672
200 ppm PMMA/clay nanocomposite	4	20.3	0.274
200 ppm PMMA	5	20.1	0.332
400 ppm PMMA/clay nanocomposite	2	17.2	0.253
400 ppm PMMA	0	18.2	0.302
800 ppm PMMA/clay nanocomposite	-3	16.2	0.178

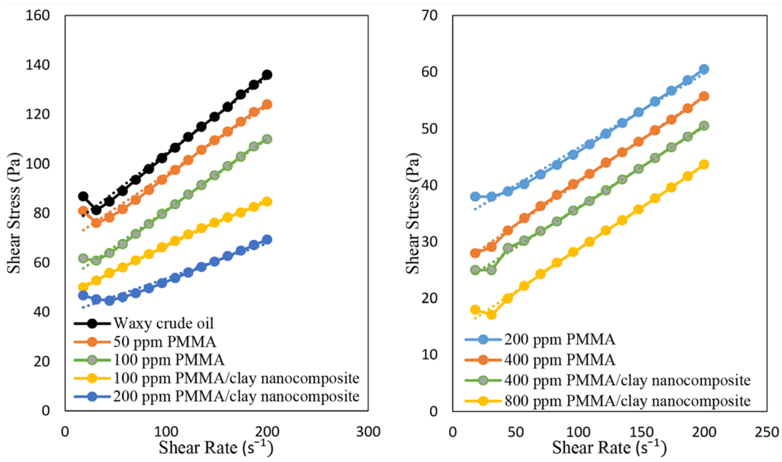


Fig. 4 Flow curves of the treated and untreated waxy crude oil at 5 °C.

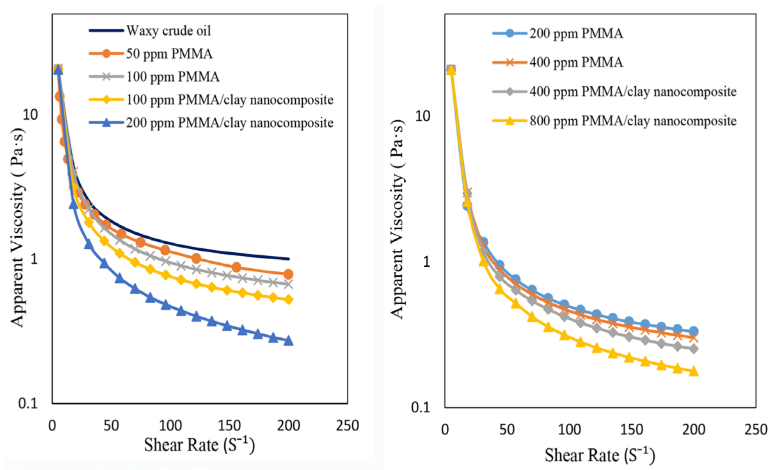
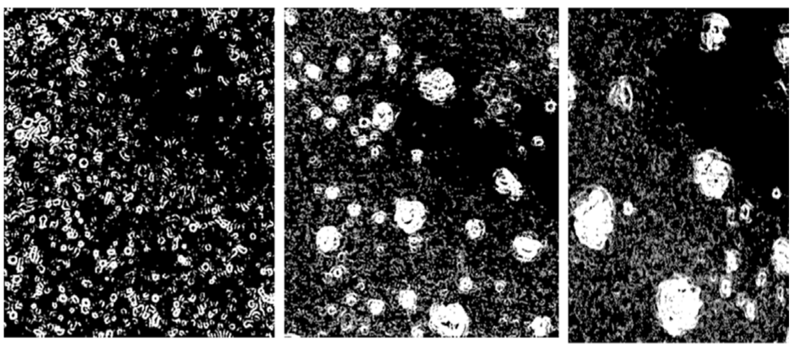


Fig. 5 Apparent viscosity versus shear rate curves of the untreated/treated waxy crude oil with the PMMA and PMMA/clay nanocomposite at 5 °C.



a) b) c)

Fig. 6 Microscopic images of the waxy crude oil at 0 ˚C: (a) Untreated sample, (b) treated with 400 ppm of the PMMA and (c) and 800 ppm of the PMMA/clay nanocomposite.

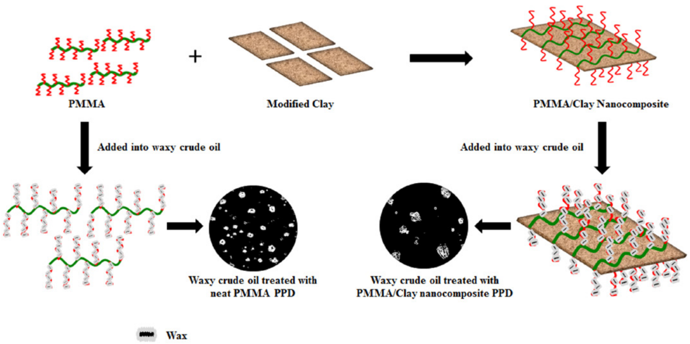


Fig. 7 Mechanistic illustration of enhancement of rheological properties of waxy crude oil treated with PMMA and PMMA/clay nanocomposite.

The enlargements of the compact waxy aggregates decrease their interfacial interactions, and thereby, the viscosity, pour point, and gelation point of the waxy crude oil are reduced, and its rheological behaviors are improved. On the other hand, the presence of the modified nanoclay layers in the PMMA/clay nanocomposite structure increases the PPD dispersity within the fluid domain, which could enhance its performance.

Conclusions

In this study, the performance of a novel polymeric nanocomposite PPD of PMMA/clay on the rheological properties of a model waxy crude oil with 20wt.% wax content was investigated comprehensively and compared with the neat PMMA efficiency. The rheological rotational and oscillatory shear tests results revealed that both PMMA and PMMA/clay nanocomposite reduced the yield stress and the gelation point of the waxy oil samples. However, the PMMA/clay nanocomposite effect was significantly higher than its rival (PMMA). Furthermore, the larger, more compact, and abundant waxy aggregates with more regular morphologies were the waxy crude oil treatment results with the PMMA/clay nanocomposite. The PMMA/clay nanocomposite changed the morphology and dispersity of the waxy solid-phase particles. The nanocomposite prevented them from forming the waxy network, thereby enhancing the rheological properties and flowability of the waxy crude oil.

Nomenclatures

PPD: Pour point depressant
PMMA: Polymethyl methacrylate
PPD: Pour point depressant
WAT: Wax appearance temperature

References

1. Pedersen KS, Rønningsen HP (2003) Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils, Journal of Energy Fuels, 17, 2: 321-328.
2. Chanda D, Sarmah A, Borthakur A, Rao K, Subrahmanyam B, Das H (1998) Combined effect of asphaltenes and flow improvers on the rheological behaviour of Indian waxy crude oil, Fuel, 77, 11:1163-1167.
3. Gilby G (1983) The use of ethylene-vinyl acetate copolymers as flow improvers in waxy crude oil, Chemical Oil Industry, 108-124.
4. Mansourpoor M, Azin R, Osfouri S, Izadpanah A (2019) Experimental measurement and modeling study for estimation of wax disappearance temperature, Journal of Dispersion Science and Technology, 40, 2:161-170.
5. Andrade DE, da Cruz AC, Franco AT, Negrão CO (2015) Influence of the initial cooling temperature on the gelation and yield stress of waxy crude oils, Rheologica Acta, 54, 2:149-157.
6. Chen W, Zhao Z, Yin C (2010) The interaction of waxes with pour point depressants, Fuel, 89, 5:1127-1132.
7. Merino-Garcia D, Correra S (2008) Cold flow: A review of a technology to avoid wax deposition, Petroleum Science and Technology, 26, 4:446-459.
8. Tiratsoo JN (1992) Pipeline pigging technology, 2nd ed., Gulf Professional Publishing, 1-12.
9. Xu J, Xing S, Qian H, Chen S, Wei X, Zhang R, Li L, Guo X. (2013) Effect of polar/nonpolar groups in comb-type copolymers on cold flowability and paraffin crystallization of waxy oils, Fuel, 103: 600-605.
10. Behbahani TJ (2014) Experimental investigation of the polymeric flow improver on waxy oils, Petroleum and Coal, 56, 2:139-142.
11. Al-Sabagh A, El-Hamouly S, Khidr T, El-Ghazawy R, Higazy SA (2013) Synthesis of phthalimide and succinimide copolymers and their evaluation as flow improvers for an Egyptian waxy crude oil. Egyptian Journal of Petroleum, 22, 3:381-393.
12. Mansourpoor M, Azin R, Osfouri S, Izadpanah AA, Saboori R (2019) Experimental investigation of rheological behavior and wax deposition of waxy oil–disulfide oil systems. Natural Resources Research, 28, 4:1609-1617.
13. Solaimany Nazar AR, Salehi N, Karimi Y, Beheshti M, Kasra Kermanshahi R (2018) Assessing the biological inhibitors effect on crude oil wax appearance temperature reduction, Journal of Petroleum Science and Technology, 8, 2:70-85.
14. Machado AL, Lucas EF, González G (2001) Poly (ethylene-co-vinyl acetate)(EVA) as wax inhibitor of a

Brazilian crude oil: oil viscosity, pour point and phase behavior of organic solutions, Journal of Petroleum Science and Engineering, 32, 2-4:159-165.
15. 15. Kuzmić AE, Radošević M, Bogdanić G, Srića V, Vuković R (2008) Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives, Fuel, 87, 13-14:2943-2950.
16. Jin M, Zhong Q (2012) Structure modification of montmorillonite nanoclay by surface coating with soy protein, Journal of Agricultural and Food Chemistry, 60, 48:11965-11971.
17. Liu SM, Yan BB, Wang P (2012) Studied on preparation montmorillonite modified by CTAMB and adsorption performance on nitrobenzene, Advance Material Research, 557:996-1004.
18. Wang F, Zhang D, Ding Y, Zhang L, Yang M, Jiang B, Zhang S, Ai M, Liu G, Zhi S, Huo L (2011) The effect of nanohybrid materials on the pour-point and viscosity depressing of waxy crude oil, Chinese Science Bulletin, 56, 1:14-17.
19. Yang F, Paso K, Norrman J, Li C, Oschmann H, Sjöblom J (2015) Hydrophilic nanoparticles facilitate wax inhibition, Energy & Fuels, 29, 3:1368-1374.
20. Yao B, Li C, Yang F, Sjöblom J, Zhang Y, Norrman J, Paso K, Xiao Z (2016) Organically modified nano-clay facilitates pour point depressing activity of polyoctadecylacrylate, Fuel, 166: 96-105.
21. Li N, Mao G, Wu W, Liu Y (2018) Effect evaluation of ethylene vinyl acetate/nano-montmorillonite pour-point depressant on improving the flow properties of model oil. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 555:296-303.
22. Giannelis EP. Polymer layered silicate nanocomposites (1996) Advanced Materials, 8, 1:29-35.
23. He H, Ding Z, Zhu J, Yuan P, Xi Y, Yang D (2005) Thermal characterization of surfactant-modified montmorillonites, Journal of Clays and Clay Minerals, 53, 3:287-293.
24. Kok MV, Létoffé J-M, Claudy P, Martin D, Garcin M, Volle J-L (1996) Comparison of wax appearance temperatures of crude oils by differential scanning calorimetry, thermomicroscopy and viscometry, Fuel, 75, 7:787-790.
25. Yang F, Li C, Wang D (2013) Studies on the structural characteristics of gelled waxy crude oils based on scaling model, Journal of Energy and Fuels, 27, 3:1307-1313.
26. Steffe JF (1996) Rheological methods in food process engineering, 2nd ed., Freeman press, 313-318.
27. Visintin RF, Lapasin R, Vignati E, D'Antona P, Lockhart TP (2005) Rheological behavior and structural interpretation of waxy crude oil gels, Journal of Langmuir, 21,14: 6240-6249.
28. Karimi Y, Solaimany Nazar AR (2020) An Experimental Study on Evaluation of Factors Influencing the Viscosity and Viscoelastic Properties of Waxy Crude Oil, Iranian Journal of Oil and Gas Science and Technology, 9, 1:1-15.
29. Morrison FA (2001) Understanding rheology,1st ed., Topics in Chemical Engineering, 134-140.