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Terpolymers as Flow Improvers for Mexican Crude Oils[†]

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The rheological behavior of dilute solutions from different terpolymers was investigated over a wide range of temperatures (20–45 °C) and shear rates (0.1–300 s⁻¹). The investigation focuses on the effect of three co-monomer contents, their molecular weight, the terpolymer, and the viscosity–temperature relationship of a Mexican crude oil (MCO). Terpolymers with different contents of styrene (S), *n*-butylacrylate (BA), and vinyl acetate (VA) were synthesized through semi-continuous emulsion polymerization. The composition of the terpolymers was evaluated by nuclear magnetic resonance (NMR) spectroscopy. The average molecular weight and polydispersity of the polymers were determined through size-exclusion chromatography (SEC). Both the untreated crude oil and the one treated with a solution of terpolymer exhibited non-Newtonian behavior. The results confirm that the viscosity of crude oil is reduced when the terpolymers have a high percentage of S and small amounts of BA or VA. The molecular weight of terpolymers plays a fundamental role in their performance as viscosity reducers.

Introduction

A change will be seen in the next few years regarding crude oil sources in the global market. Advances in exploration and production technologies in the petroleum industry are developing new major sources, in areas that were previously off limits for geographical, political, and technological reasons. Some of the new areas in exploitation will have a major significance in the U.S. markets, Latin America, mainly Venezuela, Canada, and Mexico.¹

Heavy oil and extra heavy oil are defined as having an American Petroleum Institute (API) gravity below 22° and 10°, respectively. API gravity is an inverse measure of the relative densities of oil liquid and water; high-gravity crude oils, such as those, are relatively thin and relatively easy to pump.

Many heavy crude oils contain high levels of sulfur, nitrogen, nickel, and vanadium and are rich in condensed polyaromatic compounds, reacting readily to form coke. In heavy crude oils, these types of compounds can lead to various problems in the recovery, transportation, treatment, and refining of crude oils.

Reducing the viscosity in the heavy crude is of utmost importance in the oil industry. Heavy crude production increases day after day, and a liable technology to lower crude oil viscosity has become urgent.

Minimizing the viscosity of the heavy crude oil turns into an important issue. Highly viscous crude oils, during extraction, have to go through some processing, e.g., gas plasticization, heat dilution, partial field upgrading, water emulsification,

lubrication, and core-annular flow, thermal cracking, or blending with lighter distillate fractions (gasoline, kerosene, naphtha, or other solvents) to let them be transported through pipelines.^{1,2} Other approaches that have been suggested to reduce viscosity in heavy crude oils include the use of aqueous anionic surfactant solutions to form low viscosity in water emulsion;³ such emulsions generally contain a rather high percentage of water, which must be removed.

The viscosity of crude oil is affected by the temperature; increasing the temperature is a common way to reduce viscosity, resulting in both an expensive and a non-acceptable procedure for reducing the viscosity of the crude oil to be carried over a rather long distance in the pipeline. Maintaining an elevated temperature of crude oil in a pipeline is extremely difficult.⁴ An increase in the production of crude oil from heavy crude oil reserves in the Sound of Campeche is expected; these reserves are intended to produce heavy crudes, with varying upgrading degrees. With such an increase of heavy crude oil sources in the near future, it looks like a suitable time to exploit new research paths for the reduction of viscosity.

A method for decreasing the viscosity of crude oil is involved with the fact of injecting crude oil, under high pressure, with a gas or a combination of gases, carbon dioxide (CO₂) or better, a combination of CO₂ and nitrogen (N₂).⁴ Several options are available including methods of electric pulses or magnetic fields to reduce the viscosity of crude oil⁵ and the use of chemical additives, such as flow improvers,^{6,7} viscosity reducer,^{8–10} pour point depressants (PPDs),^{11–14}

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etc. All of the chemical additives are very selective, meaning that not all additives are effective enough for every crude oil.¹⁵ For example, highly waxy crude oils are characterized by a high pour point, viscosity, and yield stress and exhibit non-Newtonian flow behavior below pour point temperatures. The process for extracting waxy crude oils from the oil fields is costly and complex, because the paraffin deposition causes a reduction in the production in terms of maintenance and removal of deposits already formed. Thus, chemical products known as flow improvers, crystal modifiers, and pour point reducers need to be used to reduce the apparent viscosity, the flow limit, and the pour point of oils.

An efficient polymeric additive for paraffin oils should be a linear polymer or co-polymer with pendant hydrocarbon chain groups and/or present hydrocarbon chains in the polymeric backbone. Polymeric compounds, such as polyalkyl acrylates and methacrylate co-polymers, alkyl esters of styrene–maleic anhydride co-polymers,¹⁶ ethylene–vinyl acetate co-polymers, etc., are some of the flow improvers for waxy crude oils.^{17,18} Other constituents in the crude oil, i.e., asphaltenes, resins, polar aromatics, etc., should also be considered as important factors while ascertaining the flow behavior of a crude oil. In addition, it is worth considering that some heavy Mexican crude oils (MCOs) are characterized by high viscosity, a high content of asphaltenes (> 8 wt %), a low quantity of paraffin components, appreciable amounts of sulfur (> 1.9 wt %), and a very noticeable content of vanadium and nickel.¹⁹

Flow improvers are quite important for crude oil delivery through pipelines and for high-quality oil products, with most of them polymers.^{20,21} The use of certain fluorochemical compounds having oleophobic and hydrophobic groups is carried out to reduce the viscosity of asphaltenic crude oils, optionally combined with a low viscosity diluent.⁹ Novel amine–chelate complexes are useful to highly reduce the viscosity of heavy crude oils.¹⁰ For example, some additives that reduce viscosity and gel strength in a considerable way are poor PPDs. Pre-treatment of heavy MCOs with a viscosity reducer (polymeric additives) could be a better choice because of its simplicity and economy.

This paper describes the preparation and evaluation of flow improving additives for MCO and could be regarded as a continuity of a recent paper.²² Additives were synthesized by means of free-radical emulsion polymerization using ecological initiators. A series of different additives of varying composition and average molecular weights was prepared by semi-continuous polymerization of three different monomers. The

Table 1. Polymerization Formulation Employed in the Synthesis of Emulsion Terpolymers with Different Contents of Transfer Agent

substance	main reactor (g)	feeding tank (g)
mixture of monomers	0	100
ammonium persulfate solution (4 wt %)	5	20
buffer solution (4 wt %)	25	0
Abex solution (7 wt %)	5	67
Disponil solution (7 wt %)	5	67
CTA	0	0–8
water	103	95–103

co-monomers were selected because of their potential PPD properties and the thermal degradation characteristics; two of them were used as polar co-monomers with probable paraffin-compatibilizing features. The performance of the prepared additives as viscosity reducers was tested on heavy crude oil samples from Mexican oil fields. The objective of this research was to observe whether the viscosity of heavy crude oils could be reduced by the addition of chemical compounds (polymers) with solvent, which may break down the asphaltene agglomerates and, thus, achieve viscosity reductions.

Experimental Section

Materials. The following substances were purchased and employed without further purification: styrene (S, M₁, Aldrich), *n*-butyl acrylate (BuA, M₂, Aldrich), vinyl acetate (VA, M₃, Aldrich), initiator (ammonium persulfate, APS, Fermont), buffer (sodium bicarbonate, J. T. Baker), emulsifiers (Abex 26-S, Rhodia and Disponil AES 13 IS, Cognis), the chain-transfer agent (CTA, 1-dodecanethiol, Aldrich), calibration standard for nuclear magnetic resonance (NMR) spectroscopy [tetramethylsilane (TMS), Fluka-Aldrich], and deuteriochloroform (CDCl₃, Aldrich). Distilled water was used during the experiments. Heavy crude oil was obtained from the Gulf of Mexico.

Synthesis. Random terpolymers with various molar ratios of S, VA, and BuA were synthesized by means of free-radical polymerization in water under a nitrogen atmosphere, using ammonium persulfate as the initiator at 70 ± 0.05 °C in a semi-continuous reactor. The polymerization formulation is shown in Table 1. The CTA is included in latex formulations to regulate (i.e., decrease) the average molecular weight and molecular-weight distribution of the latex polymer. Mercaptans are the most common type of CTA, as well as the most efficient.²³ A semi-continuous emulsion polymerization process was used to synthesize the additives. All monomers and reagents corresponding to the main reactor load (shown in Table 1) were introduced into the reactor. At first, the reagents corresponding to the main reactor were charged at the beginning of the polymerization, except the initiator solution. The reactor was heated at 70 °C for 10 min, and then the initiation solution was added. After 10 min, the pre-emulsified monomers (feeding tank) were added with the aid of a metering pump at $q = 6.67 \times 10^{-3} \text{ g L}^{-1} \text{ min}^{-1}$. The polymerization procedure was followed using an established procedure.²² The reagents were fed under strict starved-feed conditions (with the monomer feed rate being lower than the polymerization rate) with the aid of a metering pump.

The terpolymers were isolated by means of water evaporation and dried at room temperature, showing either yellow viscous liquid or pale yellow wax-like appearances.

Polymer Characterization. Samples for spectroscopic characterization were first precipitated from latex by the addition of a solution of 0.1 N HCl. Afterward, the dry polymer was dissolved 3 times in tetrahydrofuran (THF) and subsequently precipitated

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Table 2. Composition and Molecular-Weight Characterization of Terpolymers

polymer code	CTA (%)	PC (mol %)			M_w	M_n	I
		S	BuA	VA			
TP1	1.0	87.2	10.0	2.8	45175	21547	2.1
TP2	8.0	57.5	31.7	10.8	7245	2223	3.3
TP3	1.0	87.3	1.7	11.0	18622	6816	2.7
TP4	1.0	7.8	91.0	1.2	39204	20701	1.9
TP5	0.0	63.2	22.9	13.0	557924	139900	2.3
TP6	8.0	49.9	32.4	17.7	3785	2057	1.8

with methanol. The purified samples were finally dried in an oven at 150 °C for 24 h. ^1H NMR spectra were recorded in Jeol Eclipse-300 equipment using deuterated chloroform with TMS as an internal standard. The molecular weights and polydispersity index (I) of co-polymers were determined using a size-exclusion chromatography Agilent 1100 chromatograph with a 5 μm column of PLgel. THF, at a flow rate of 1 mL min $^{-1}$ at 30 °C, was used as the mobile phase. A calibration curve was made using the well-defined narrow molecular-weight distribution polystyrene standards kit available from Aldrich.

Additive Preparation. Polymer solutions were prepared at 20 wt % of terpolymer in toluene; each solution was stirred for 10 min at the doping temperature for homogenization. Terpolymers were mixed in the oil at 1000 ppm.

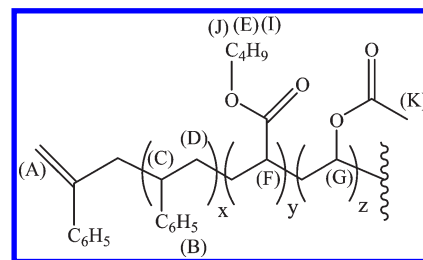
Sample Preparation. To obtain results consistent with accurate rheological measurements, the memory of the evaluated crude oil sample has to be removed by heating at 60 °C while stirring. Tests were started by heating the preconditioned untreated crude oil samples to 60 °C in an ultrasonic bath and then loading them in a hermetic bottle with an appropriate amount of solution preparation; finally, the temperature of the sample in the ultrasonic bath was maintained at 60 ± 1 °C for 30 min.

Rheological Investigation. Rheological investigation was carried out using a Physica MCR301 (Anton Paar) modular rheometer, equipped with a concentric cylinder CC27. The crude oil was examined under a shear rate range of 0.01–300 s $^{-1}$, and over a temperature range of 20–45 °C. The mathematical treatment was carried out using the computer program, Rheoplus, version 3.1, for Windows.

Results and Discussion

Molecular Characterization of the Terpolymers. Terpolymer composition was determined using the method outlined by Thamizharasi et al.²⁴ The relative peak intensities were determined from peak areas calculated by means of electronic integration. Table 2 shows the CTA content, the polymer composition (PC), average molecular weights (M_w and M_n), polydispersity (I), and degree of polymerization of the S–BuA–VA terpolymers. The chemical structure of the synthesized compounds is shown in Figure 1. It is important to mention that the conversion of the reported reactions was practically 100%; therefore, the compositions of monomer mixtures in feed are those of terpolymers.

The conventional and simplified terpolymerization equations can be used to predict the composition of a terpolymer from the reactivity ratios in the two component systems M_1/M_2 , M_1/M_3 , and M_2/M_3 .²⁵ For example, in the case of component system M_2/M_3 , the reaction is complicated because of the large differences in monomer reactivity ratios ($r_{VA} = 0.08$, and $r_{BuA} = 7.2$) and water solubility (0.291 and 0.006 mol dm $^{-3}$, respectively, at 20 °C).²³ Various attempts

**Figure 1.** Structural representation of S–BuA–VA terpolymer.

have been made to place the radical monomer reaction on a quantitative basis in terms of correlating the structure with reactivity. The Q – e scheme is the best one considered as an empirical approach for placing monomer reactivity on a quantitative basis. The average Q and e values of the three monomers used in this work are as follows: S ($Q = 1.0$, and $e = -0.80$), BuA ($Q = 0.38$, and $e = 0.85$), and VA ($Q = 0.026$, and $e = -0.88$),²⁵ therefore, ideal co-polymerization occurs between two monomers having similar Q and e values. The tendency toward alternation is highest for monomers having the same Q values with high e values of opposite sign. In summary, the reactivity ratios of the monomers employed in this synthesis are different, modifying in turn the terpolymer structure. Nevertheless, homogeneous terpolymerizations are obtained under monomer-starved conditions in semi-continuous processes independent of reactivity values.

The free-radical polymerization, employed in many industrial processes, consists of three stages: initiation, propagation, and termination. The propagation processes can proceed on a continuous basis, while some termination processes take place. There are two different termination manners: disproportionation and combination. Two radicals react with each other by means of combination (coupling), or when two propagating radicals P_m and P_n meet, they can transform into two inert polymers, respectively, with m and n repeating units as a result of disproportionation, in which a hydrogen radical that is β to one radical center is transferred to another radical center. These termination mechanisms result in the formation of two kinds of polymer molecules: a saturated molecule and an unsaturated molecule.²⁵

The spectroscopical characterization of the synthesized terpolymers seems to indicate both different termination manners, because after an exhaustive terpolymer purification, the signal of the double bond is present in the ^1H spectra. The formation of the double bond at the chain end is clear evidence of a termination mechanism by disproportionation. The coexistence of free-radical propagation and disproportionation has been reported in the literature, and it has been remarked that both proceed at constant rates, especially in the case when S is employed.^{26,27} Predominance of a termination mechanism mainly depends upon the M monomers chemical structure and polymerization temperature.²⁸

Figure 2 shows the stacked plot of the ^1H NMR spectra of the synthesized S–BuA–VA terpolymers, and the assignments of the different peaks are given in Table 3.

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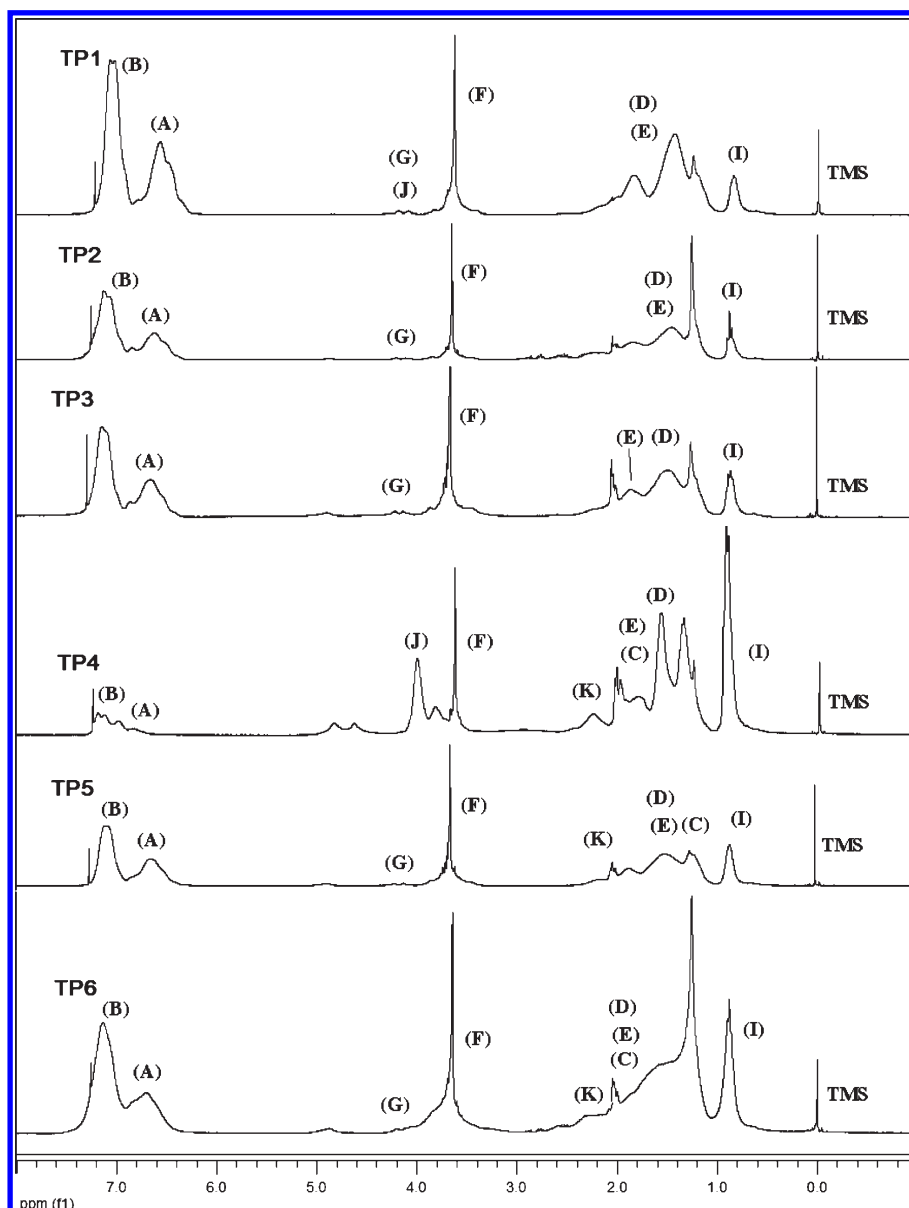
Figure 2. ^1H NMR for terpolymers.

Table 3. Peak Assignments for Different Functional Groups

ppm	assignment
7.13	aromatic ring proton
6.4–6.6	olefinic proton
4.1	(–OCH–)
3.9	(–OCH ₂ –)
2.0	(–CO–CH ₃)
1.2–1.8	(–CH ₂ –)
0.9	(–CH ₃)

Rheological Studies. The physical characteristics of crude oil evaluated in this research are given in Table 4. This MCO is heavy, and its asphaltene content is 19.92%, which is mainly responsible for its great viscosity and influences its flow behavior strongly.

The apparent viscosity of MCO was determined at different additive concentrations and temperatures using a Physica MCR301 rheometer. A rheogram of MCO is shown in Figure 3. If the shear stress is not proportional to the shear rate, then such ratios ($\tau/\dot{\gamma}$) are often called the “apparent

Table 4. Physical Characterization of Crude Oil¹⁹

specification	heavy crude oil	methods
API density	15.82	ASTM D-287
water by distillation (vol %)	0.10	ASTM D-4006-07
kinematic viscosity at 25 °C (mm ² s ^{−1})	2984.97	ASTM D-445
asphaltene content (wt %)	19.92	ASTM D-2007

viscosity” or “apparent shear viscosity”, not necessarily being constant according to ASTM D4092 and DIN 1342-1. The viscosity values obtained are apparent and represent one point if the viscosity function only.^{29,30} It is clearly seen that, at 20 °C, the shear rate against the shear stress curve (flow curve) does not pass through the origin. The apparent viscosity is not a constant at different values of shear rate (viscosity curve). The crude oil viscosities at shear rates

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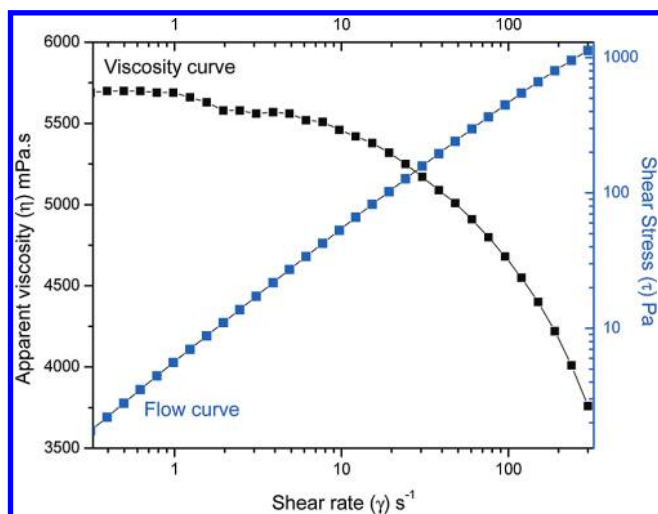


Figure 3. Rheogram of the MCO sample at 20 °C.

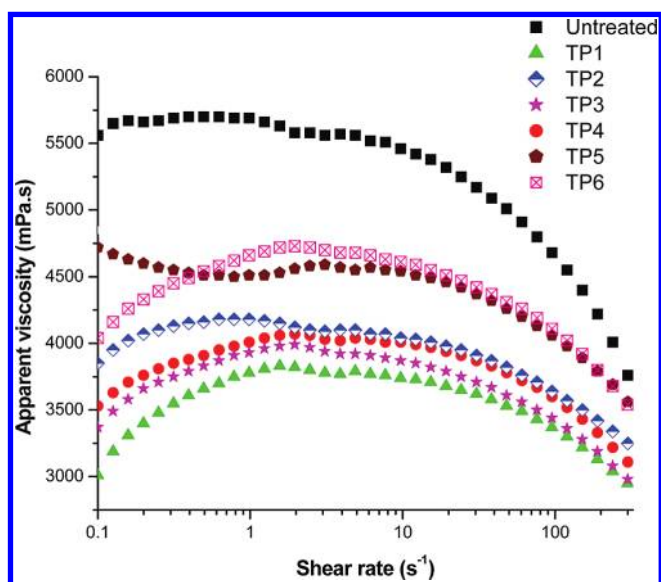


Figure 4. Apparent viscosity of heavy crude oil containing 1000 ppm of terpolymer solution as a function of the shear rate at 20 °C.

between 0.1 and 3 s^{-1} are not so different. It is obvious that, by increasing the shear rate, the apparent viscosity decreases dramatically (e.g., from 5578 mPa s at 2 s^{-1} to 3770 mPa s at 300 s^{-1}) at 20 °C. This behavior corresponds to that of a “non-Newtonian” fluid.³¹

Effect of the Molecular Composition and Molecular Weight on Apparent Viscosity. Figure 4 shows representative plots of shear rate ($\dot{\gamma}$) versus apparent viscosity (η) of heavy crude oil containing 1000 ppm of terpolymer solution at 20 °C. Paraffin crystals have already been formed at this temperature in the liquid, and the rheological behavior of the crude oil is non-Newtonian. The untreated crude oil and that containing polymer solutions are clearly non-Newtonian “pseudo-plastic liquids”, and the flow behavior cannot be explained by simple Newtonian behavior. It is important to remark that there was no difference between the curves of the untreated crude oil and that of the crude oil used as an additive with 1000 ppm of toluene (solvent). The decrease of

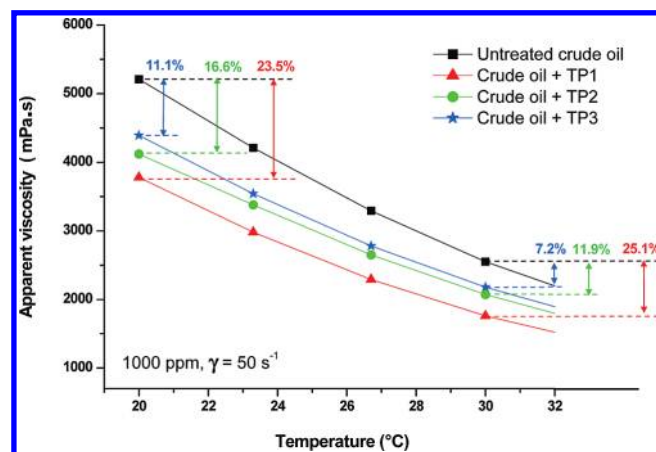


Figure 5. Temperature effect on the apparent viscosity of the heavy crude oil. The crude oil was used as an additive with 1000 ppm of terpolymer solutions.

viscosity, when the shear rate is increased, is more evident at low temperatures because of the larger polymer molecular orientation, resulting from larger shear forces acting on the polymer and the crude oil under these conditions. As mentioned in the literature, viscosity of crude oils decreased as the shear rate increased.³²

It was observed that all terpolymers diminish the crude oil apparent viscosity and reductions strongly depend upon molecular weight and composition of the terpolymer used as an additive. The apparent viscosity of the crude oil used as an additive with polymer solutions depends upon the average molecular weight (molecular chain length), temperature, and thermodynamic interaction between polymer chain segments and crude oil molecules. The performance as the viscosity reducer of a polymer, with an adequate molecular weight and composition, mainly depends upon its thermodynamic affinity to the components of crude oil (saturates, resins, asphaltenes, and aromatics). For example, the polymer samples TP6 and TP5, with very different molecular weights and almost similar composition, exhibit practically the same performance as apparent viscosity reducers. However, they are not the best rheological modifiers. In a similar way, terpolymers TP2 and TP4, with different molecular weights and different product compositions, exhibit the same flow behavior, after a shear rate of 2 s^{-1} . In contrast, TP3 and TP1, with a rich S composition, both show the greatest falls of apparent viscosity through the range of shear rate. The viscosity curve corresponding to the crude oil used as an additive with a TP1 solution exhibited the most considerable reduction of apparent viscosity through the shear rate range, and the curve has the same shape as that of the untreated crude oil but at lower viscosity values. An analysis of the influence of the terpolymer composition on the rheological behavior of the crude oil used as an additive reveals that, the higher the content of S, the greater the viscosity reduction, independent of the polymer molecular weight. The performance of a terpolymer as a flow improver may be explained taking into account the following structural effects: (1) S allows for better interactions with asphaltenes, resins, and other compounds because of its aromatic nature, (2) VA, conferring polar functionality to the terpolymer backbone, lead to the creation of attractive forces between the additive

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and resins, and (3) BuA units promote interactions between terpolymers and paraffins in crude oil.

The molecular weight of the polymeric additive plays an important role in the reduction of petroleum viscosity; however, the terpolymer structure, composition, and solubility in crude oil are also very important. It was also observed that terpolymers with an average molecular weight in an interval between 22000 and 2000 Da showed best performances as flow improvers in petroleum.

Effect of the Temperature on Viscosity. Figure 5 shows the results of both untreated and treated MCO viscosity versus temperature, for a TP1, TP2, and TP3, in which the samples were examined at a shear rate ($\dot{\gamma}$) of 50 s^{-1} and over a temperature range of 20–45 °C. Also, Figure 5 clearly shows that the addition of terpolymers causes viscosity reduction, being more evident between 20 and 30 °C (Figure 5), corresponding to the temperature range of transportation in ducts for this type of MCO.

Figure 5 shows the apparent viscosity behavior of both untreated and treated crude oil with terpolymers from 20 to 30 °C. The TP1 terpolymer is the best additive for reducing viscosity, sensibly improving the flow. Indeed, crude oil with the TP1 agent presents 23.5% of viscosity reduction at 20 °C and 25.1% of viscosity reduction at 30 °C. It is possible to compare viscosity reductions of the best three terpolymers in the same figure.

Mechanism of Viscosity Reduction. Some authors claim that higher viscosity of crude oils is due to the presence of hydrogen bonds and the overlapping of aromatic ring planes among resins and asphaltene molecules in it.^{33,34} In general, higher amounts of resins and asphaltenes in crude oil increase the apparent viscosity. Thus, to reduce crude oil viscosity, the hydrogen bonds existing between resins and asphaltene molecules have to be broken. The structure of the

terpolymer added to the crude oil creeps up among the hydrogen bonds between asphaltenes and resins, creating spaces and, thus, reducing the apparent viscosity of heavy crude oil.

Conclusions

A series of effective terpolymer additives for improving the flow of heavy MCO was synthesized by semi-continuous emulsion polymerization. These polymeric additives were characterized by spectroscopic and size-exclusion chromatography (SEC) methods. The terpolymers were added to the MCO, and their effects on the rheological properties of this heavy crude oil were investigated. All of the terpolymers satisfied the requirements of flow improvers. The introduction of a small quantity of polar co-monomer (BuA or VA) in the terpolymer backbone has an effect on the reduction of apparent viscosity in this type of heavy crude oil.³⁵ In contrast, the addition of a great quantity of S as a component of the terpolymer shows a conclusive effect on the flow improvement of petroleum. The importance of choosing an adequate molecular weight of the polymer additive was also witnessed.

Both the untreated crude oil and the treated crude oil with terpolymers show non-Newtonian behavior over a wide range of shear rates and temperatures. The apparent viscosity results confirm that the TP1 terpolymer, with an adequate molecular weight and a high S content, improves the crude oil flow. Consequently, the molecular weight and monomer composition were revealed as key molecular parameters to control the performance of a flow improver.

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