Synthesis of comb-type copolymers with various pendants and their effect on the complex rheological behaviors of waxy oils

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ABSTRACT: To improve the flowability of waxy crude oil containing a high concentration of asphaltenes (AS), novel comb-type copolymers of poly(maleic acid polyethylene glycol ester-co-α-octadecene) (PMAC) and poly(maleic acid aniline amide-co-α-octadecene) (AMAC) with various grafting ratios (R_g) of PEG/aniline to maleic anhydride are synthesized. Model oils containing wax mixtures and AS are prepared to explore the effect of asphaltene concentration and the copolymers on the yield stress. The influence of the copolymers on the wax appearance temperature (WAT) of Liaohe high waxy oil is examined by rheological and microscopic methods. Experimental flow curves of shear stress as a function of shear rate are fitted following the Casson model to interpret the rheological properties of gelled waxy crude oil in the presence of AMACs, PMACs, and MAC. Compared with MAC, PMACs, and AMACs are more efficient in reducing the yield stress of both model oil and crude oil, which indicates a better flowability. It is found that PMAC1.0 and AMAC1.0 with a medium R_g can balance the interaction of copolymers with waxes and AS and reduce the yield stress much more than others. Between them, AMAC1.0 that possesses aromatic pendants is better than PMAC1.0, which only has polar pendants. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41660.

INTRODUCTION

Paraffinic alkanes are known to precipitate from waxy crude oil when the temperature drops below the wax appearance temperature (WAT).[1,2] As the temperature keeps decreasing, a dramatic increase of viscosity could be observed inside the oil pipeline, which may lead to a partial or complete blockage of the pipes and impose extra burden on the pumping systems.[3–5] Specifically, in the case of offshore oil delivery or transportation in cold regions, wax precipitation may cause severe problems since the oil restarting in the pipeline usually is difficult to implement. Several methods have been employed to remediate these problems, including heating, mechanical pigging, and blending the crude oil with gasoline or kerosene.[6] Nowadays, blending crude oil with low concentration of polymer additives appears to be a more effective way of solving those problems caused by wax precipitation. Several kinds of comb-type polymer additives such as poly(ethylene-butene) (PEB)[7,8] and poly(maleic anhydride-co-α-olefin) derivatives (MAC)[9–14] have been reported as cold flow improvers for waxy oil.

A comprehensive evaluation of the effect of polymer additives on enhancing oil transportability usually depends on an intensive understanding of the rheology and crystallization behaviors of wax in waxy oil. Fitting the flow curves by rheological models serves as an important mathematical approach to researching the rheological properties of the crude oil. Many researchers have proposed models for both the flow behaviors of waxy oils and the deposition of wax during oil transportation.[15–17] Mathematical models for the flow behaviors of waxy oils, which are assumed to behave as the non-Newtonian Bingham fluids are proposed.[16] The Casson model has been promoted by combining itself with the Richardson model, which is applied to fit the viscosity-shear rate curves of North Sea oil samples in order to predict the viscosity of oil at certain temperature and shear rate.[17]

In this work, two novel comb-type copolymers, poly(acid polyethylene glycol ester-co-α-octadecene) (PMAC) and poly(maleic acid aniline amide-co-α-octadecene) (AMAC), are synthesized by chemical grafting polyethylene glycol (PEG) and aniline into poly(maleic anhydride-co-α-octadecene) copolymer. The effect of copolymers with polar and aromatic pendants on the cold flow ability of Liaohe high waxy oils is studied by rheological method and optical microscopy. Interaction between copolymers and

Table I. Composition of the Prepared Model Oils

AS (%)	1-MN (%)	C36 (%)	C32 (%)	Decane (%)	Polymers (%)
0.0	33.0	4.0	4.0	59.0	0
0.1	33.0	4.0	4.0	58.9	0
0.5	33.0	4.0	4.0	58.5	0
0.7	33.0	4.0	4.0	58.3	0
1.0	33.0	4.0	4.0	57.5–58	0, 0.1, 0.3, 0.5

asphaltenes (AS) and its effect on the rheology of waxy oil are researched. To interpret the effect of copolymers and AS on the rheological behaviors of waxy oils, the Power law, Bingham and Casson model are chosen to fit the rheological curves. The fitting results are compared to each other in order to choose a suitable model to predict the rheological behaviors of high waxy oil.

EXPERIMENTAL

Materials

Decane (>99%), maleic anhydride (99%), α-octadecene (95%), aniline (99%), heptane (>99%), benzoyl peroxide (99%), o-xylene (98%), and octadecylamine (97%) are purchased from Alfa-Aesarcompany. Hexatriacontane (>98%), dotriacontane (>98%) 1-methylnaphthalene (97%) are purchased from Sigma Aldrich. PEG200 (99%) are purchased from Shanghai National Chemical Reagent Company. All the chemicals are used as obtained.

Waxy crude oil sample, which has been dehydrated before using, is obtained from Petrochina Liaohe Oilfield. The content of paraffin and AS are 38.5% and 15.6%, respectively. The density, freezing point, and viscosity at 70°C are 0.8676 g/cm^3, 57°C and 7.2 mPa s, respectively.

Synthesis and Characterization of Copolymers

All of the copolymers are synthesized by two steps. In the first step, maleic anhydride and α-octadecene are dissolved in o-xylene with benzoyl peroxide as an initiator, polymerized at 120°C for 1.5 h under nitrogen protection, then poly(maleic anhydride-co-α-octadecene) is obtained.[11,18] In the second step, aniline or PEG200 is fed in and reacts with the maleic anhydride group in poly(maleic anhydride-co-α-octadecene) at 65°C for 12 h. Then crude products are purified by precipitation in methanol, washed by hot water after filtration, and dried by freeze-drying. The obtained copolymers are named AMAC and PMAC, respectively. By varying the feeding ratios of aniline or PEG200 to maleic anhydride which is 0.5, 1.0, and 1.5, two series of comb-type copolymers are obtained, named AMAC0.5, AMAC1.0, AMAC1.5, and PMAC0.5, PMAC1.0, PMAC1.5. In our previous work, poly(maleic anhydride-co-α-octadecene) aminated by octadecylamine (MAC) with various ratio of octadecylamine to maleic anhydride has been synthesized,[11] which will be compared with both AMAC and PMAC.

The chemical structure and grafting ratio of copolymer are confirmed by ^{1}H NMR. ^{1}H NMR spectra are recorded on a Bruker DRX500 at 500 MHz with deuterated chloroform as a solvent.

Preparation of Model Oil

First, dotriacontane (C32) and hexatriacontane (C36) are dissolved in decane. AS, which is extracted from Liaohe crude oil is dissolved in 1-methylnaphthalene (1-MN). Then, a combination of the above two solutions is mixed vigorously by strong stirring. Model oil samples are prepared by feeding different copolymers into the mixture solution and heated to 80°C under stirring to ensure that the copolymers are fully dissolved. All of the model oil samples are prepared before subsequent testing. The components of the model oils are listed in Table I.

Molecular Weight and Molecular Weight Distribution of Copolymers

The molecular weight and molecular weight distribution of the poly(maleic anhydride-co-α-octadecene) are measured by a Waters 1525 GPC instrument with tetrahydrofuran as the mobile phase and polystyrene samples as standards.

Rheological Measurements

All rheological measurements are performed on a Physica MCR501 rheometer (Anton Paar Company, Austria) equipped with a 25 mm parallel plate geometry. The temperature of the plate is controlled within ±0.1°C by a Peltier plate. A hood is used to prevent the solvent from evaporation. The liquid samples are accommodated using a measuring cell mounted on top of the lower Peltier plate. A 1 mm gap is employed in all measurements.

Before loading on the rheometer, oil sample is heated to 90°C in a sealed cup for 15 min to ensure that the paraffins and copolymers are completely dissolved. Then a 2.5 mL of oil sample is loaded on the preheated parallel plate. Once the parallel plate is descended, the hood is covered to minimize the loss of solvent. Before the start of all tests, the sample is held at 90°C on the plate for at least 5 min to equilibrate the temperature.

The yield stress here is defined as the stress below which the oil will not flow, which is able to be measured following our previous work.[19] The sample is cooled from 90°C to the testing temperature (0°C for the model oil and 30°C for the crude oil) and then held at that temperature for 20 min. The stress is then increased stepwise logarithmically, with 20 stress levels per decade and 8 s per data point. The initial stress is usually 0.01 Pa and the rheometer is programmed to stop the test when a comparatively high shear stress is reached, which is higher than the yield stress of the sample and is usually 1600 Pa. The stress where the viscosity drops sharply from a high value is recorded as the yield stress.

The relationship between shear stress and shear rate of the oil samples are measured using the following sequence: oil sample is loaded on the measuring cell and then cooled from 90°C to the testing temperature. The shear stress is subsequently recorded with the shear rate logarithmically increasing from 0.01 to 2000 s^{-1}. Each curve consists of 51 measuring points with its measuring point duration varying from 50 to 5 s.

The WAT is defined as the temperature at which precipitated paraffin crystals can be found. The pseudoplastic fluids, such as Casson[20] or Herschel–Bulkley[21] fluid, usually transfer from the Newtonian fluids to the non-Newtonian fluids when the temperature drops below the WAT. Crude oil samples in the
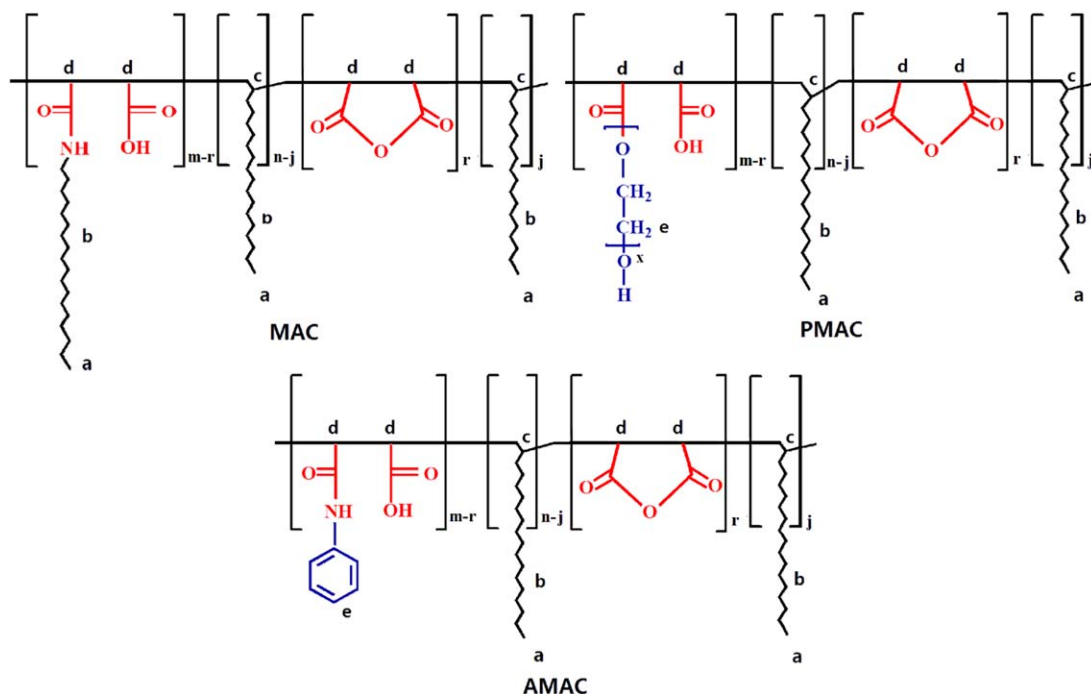
Figure 1. Chemical structure of PMAC, AMAC, and MAC copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absence and presence of copolymers are cooled from 65 to 45°C at a constant cooling rate under the shear rate of 10 s^{-1}, and their viscosity is recorded as a function of temperature. WAT is determined by extrapolating the viscosity-temperature curve above this critical temperature, and the relationship between viscosity and temperature can be described by Arrhenius equation at the temperature above the WAT.

Optical Microscopy

The morphology of paraffin crystallites is observed using a LEI-KADM 2500P PLM with a Linkam THMS 600 cold/hot stage. Micrographs are obtained using a charge-coupled device camera attached to the microscope with a WT-1000GM imaging board. A small quantity of waxy crude oil sample is transferred from storage

to a glass slide on the cold/hot stage for observation. Oil samples are heated to a temperature of 70°C, which is above the WAT, and held at this temperature for 20 min to eliminate any thermal history. Then the samples are cooled to 50°C at a cooling rate of 0.5°C/min to ensure being fully gelled. Images are taken at the temperature near the WAT to observe the growth of paraffin crystals.

RESULTS AND DISCUSSION

Chemical Structure, Grafting Ratio, and Molecular Weight of Copolymers

The chemical structures of the synthesized copolymers are shown in Figure 1. The chemical structures of PMAC and

Table II. Chemical Shift of Protons in Copolymers

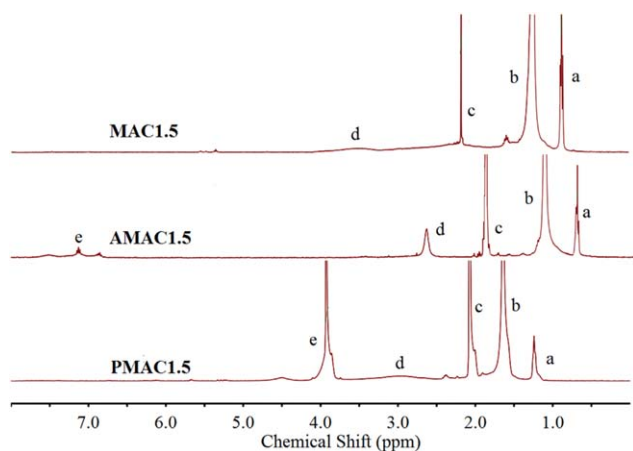| Polymer	Proton	Chemical shift (ppm)
AMAC	CH$_3$ (a)	1.0
	CH$_2$ (b)	1.2
	CH (c)	1.9
	CCH (d)	3.2
	ArH (e)	7.2
PMAC	CH$_3$ (a)	1.2
	CH$_2$ (b)	1.6
	CH (c)	2.1
	CCH (d)	2.9
	OCH$_2$ (e)	3.9
MAC	CH$_3$ (a)	0.9
	CH$_2$ (b)	1.2
	CH (d)	3.4
	CCH (d)	2.7

Figure 2. ^{1}H NMR spectra of MAC1.5, AMAC1.5, and PMAC1.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The Feeding Ratio (R_f) and the Grafting Ratio (R_g) of the Pendants in PMAC, AMAC, and MAC

Polymer	R_f^*	R_g^*	A_x^*
AMAC0.5	0.5	0.31	4.84
AMAC1.0	1.0	0.76	11.9
AMAC1.5	1.5	0.98	15.3
PMAC0.5	0.5	0.26	13.0
PMAC1.0	1.0	0.68	34.0
PMAC1.5	1.5	1.08	54.0
MAC	1.5	1.1	32.6

R_f and R_g represent the feeding ratio and the grafting ratio of the pendants, respectively. A_x represents $A(C_6H_5)$ for AMAC, $A(OCH_3)$ for PMAC, and $A(CH)$ for MAC.

AMAC copolymers are characterized by ^1H NMR spectra (Figure 2). The chemical shift of protons in each copolymer is determined and is listed in Table II. According to the ^1H NMR results, both novel copolymers have been successfully synthesized.

The integration of the protons in poly(maleic anhydride-*co*-α-octadecene) reveals that the copolymerization ratio of maleic anhydride/α-octadecene is 1 : 1.07. The grafting ratios (R_g) are calculated through integrating the peak area of protons in oxyethyl, benzonic rings, and methyl groups in octadecene monomeric unit. The integration of protons in methyl group $A(CH_3)$ around 1.0 ppm are set at 10. The R_g for AMACs is calculated by the equation $R_g = \frac{3.2A(C_6H_5)}{5A(CH_3)}$. The integration of protons in benzoic groups $A(C_6H_5)$ for AMAC0.5, AMAC1.0, and AMAC1.5 are 4.84, 11.9, and 15.3, respectively. Then the corresponding grafting ratios are calculated out, which are 0.31, 0.76, and 0.98, respectively. Similarly, the R_g for PMACs is calculated using the equation $R_g = \frac{3.2A(OCH_3)}{16A(CH_3)}$ and the R_g for MAC is calculated using the equation $R_g = \frac{2A(CH)}{3A(CH_3)} - 1.07$, in which $A(OCH_3)$ refers to the integration of protons in the oxyethyl pendent in PMACs and $A(CH)$ refers to the integration of protons in CH groups in the MAC backbone. The integration of protons in each group for calculation and the calculated grafting ratio (R_g) are listed in Table III. It is found that the calculated grafting ratios (R_g) are not the same with the feeding ratios (R_f), but are increased with the increase of R_f.

The molecular weight of poly(maleic anhydride-*co*-α-octadecene) for the synthesis of PMAC, AMAC and MAC is measured by GPC, which is 3.62 kg/mol, and the distribution of molecular weight is 1.12.

Effect of Asphaltenes and Copolymers on Model Oils
The effect of AS concentration on the yield stress of model oil in absence of copolymers has been investigated, as shown in Figure 3. From this Figure, it is found that the yield stress of model oil decreased from 64.9 to 60.4 Pa by the presence of 0.1 wt % of AS and to 55.0 Pa by the presence of 0.3 wt % of AS. This result supports the opinion that AS are able to disperse wax crystals during the cooling process at a low concentration.[22] However, if the concentration of AS is above 0.3 wt %, the yield stress of gelled model oil begins to increase. When the concen-
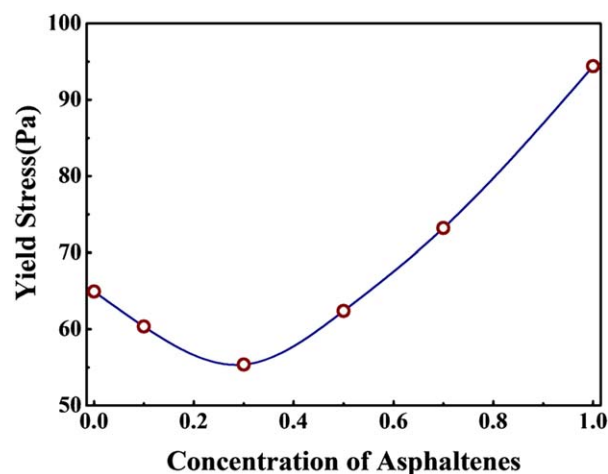
Figure 3. The change of yield stress of model oils upon the increase of asphaltene concentration at 0°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tration of AS rises from 0.3 to 1.0 wt %, the yield stress is increased from 64.9 to 94.4 Pa, which is consistent with the other research.[23] This phenomenon is probably due to that large asphaltene aggregates, which are poorly dispersed at a high concentration may serve as nucleation sites and benefit the growth of wax crystals.[22]

The influence of different pendants in copolymers on the yield stress of model oils has been investigated, as shown in Table IV. The yield stress of model oil with 1 wt % AS and without any copolymer is 94.4 Pa. From Table IV, it is found that both PMAC and AMAC copolymers effectively reduce the yield stress of model oils. For model oil in the presence of PMACs with various grafting ratios, the yield stress decreases with the increase of polymer concentration. After the dosage of PMAC1.0, which has a moderate grafting ratio ($R_g = 0.68$), the yield stress of model oil is reduced much more than that after the dosage of PMAC0.5 ($R_g = 0.26$) and PMAC1.5 ($R_g = 1.08$). In presence of PMAC1.0 at a concentration of 0.5%, the yield stress is reduced by 96.8%, which is the largest reduction for all

Table IV. The Effect of Grafting Ratio and Concentration of Copolymers on the Yield Stress of Model Oils with 1 wt % Asphaltene

Copolymer	Grafting ratio (R_g)	Yield stress (Pa)[a]		
		0.1%[b]	0.3%[b]	0.5%[b]
PMAC0.5	0.26	12.4	8.1	5.0
PMAC1.0	0.68	8.5	5.0	3.0
PMAC1.5	1.08	10.2	7.1	4.2
AMAC0.5	0.31	13.4	8.4	4.6
AMAC1.0	0.76	7.1	2.5	4.2
AMAC1.5	0.98	12.5	7.1	3.0
MAC1.5	1.10	14.4	10.0	6.0

[a] The yield stress of model oil containing 1 wt % asphaltene and in absence of copolymers is 94.4 Pa
[b] 0.1 wt %, 0.3 wt %, and 0.5 wt % are the concentration of copolymer in oils.
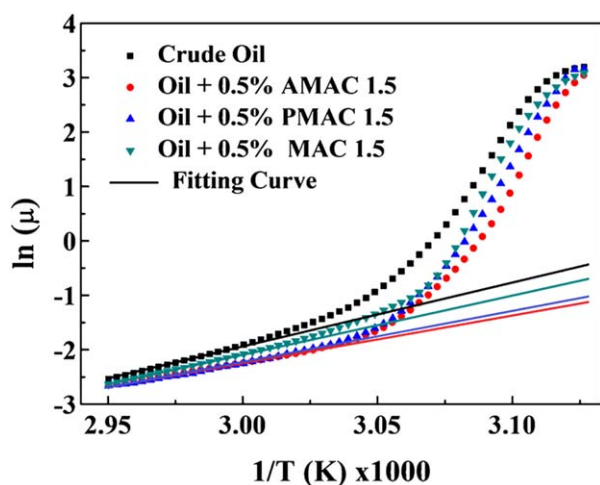
Figure 4. The dependence of temperature on the viscosity of crude oil samples in the absence and presence of copolymers. The dotted lines are the rheological data, and the solid lines are the fitting lines following the Arrhenius Equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PAMCs at any concentration. Therefore, there is a proper grafting ratio for PMAC to achieve the largest reduction of yield stress.

Similarly, in the case of AMAC, although the yield stress of model oil in presence of AMAC1.5 ($R_g = 0.98$) is slightly lower than that in presence of AMAC1.0 ($R_g = 0.76$) at the concentration of 0.5%, the yield stress in presence of AMAC1.0 is much lower than that in presence of AMAC0.5 ($R_g = 0.31$) and AMAC1.5 at the concentration of 0.1 and 0.3 wt %. The yield stress is reduced by 97.4% in presence of AMAC1.0 at a concentration of 0.3 wt %, which is also the highest reduction for all copolymers and concentrations tested. It is also found that the yield stress drops with the increase of polymer concentrations. However, when the concentration of AMAC1.0 is increased from 0.3 to 0.5 wt %, the yield stress is increased from 2.5 to 4.2 Pa, indicating that the yield stress is not always reduced by the increase of the polymer concentration.

As shown in Table IV, the grafting ratio of copolymers has an obvious effect on the yield stress. The reduction of yield stress of model oil is not the largest in presence of the copolymers with the highest grafting ratio. Generally, copolymers with close grafting ratios have similar reduction in the yield stress. However, the reduction of yield stress of model oil in presence of MAC1.5 is apparently lower than that in presence of AMAC1.5 and PMAC1.5 at all of the concentrations, indicating that the introduction of aromatic and polar pendents benefit for the reduction of yield stress for model oil containing AS.

Rheological Behaviors and Modeling of Waxy Crude Oil

The effect of temperature on the viscosity of Liaohe waxy crude oils is researched, as shown in Figure 4. The Arrhenius Equation is applied to evaluate the dependence of temperature on the viscosity by fitting the rheological curves of crude oils. In the case of oil in absence of copolymer, the rheological curve obeys the Arrhenius Equation at temperatures above 332 K. In presence of copolymers, the WAT of crude oil is reduced by 1.0–2.5°C. In

another word, these copolymers depress the precipitation of wax to some degree. It is found that the reduction of WAT is larger in the presence of AMAC1.5 and PMAC1.5 than that in the presence of MAC1.5. It is probably because that PEG and benzonic pendants benefit for the copolymers being adsorbed on the surface of AS since AS are the most polar and aromatic components in crude oil. This in turn disturbs the crystallization of paraffins.

During cooling and at temperatures close to the WAT, the viscosity of tested crude oil is increased with the decrease of temperature, which is able to be fitted following the Arrhenius Equation:

$$\text{Arrhenius Equation} : \mu = \mu_0 e^{\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \quad (1)$$

Here μ_0 is the viscosity of the oil at temperature T_0 which is 45°C in this work, E_a is the activation energy for the measured fluids. The WAT is determined as the temperature under, which the behaviors of crude oil cannot be predicted by Arrhenius Equation. For example, the WAT of crude oil in absence of copolymers is 332 K (59°C). When the temperature drops below 59°C, the fitting lines following Arrhenius Equation show an apparent deviation from the rheological data. The related parameters are listed in Table V.

The non-Newtonian behaviors of waxy oils below WAT are attributed to the waxy gels formed by precipitation of wax, which can be observed by polarizing light microscope (PLM) equipped with a cooling stage. Figure 5 shows the microphotos of crude oil sample in the absence of copolymers taken during cooling and across the WAT. Small wax crystals begin to emerge when the temperature reaches 60°C, at a higher temperature than which no wax precipitates can be observed. As the oil sample is further cooled, more wax crystals appear and gradually grow into larger ones.

Microscopic morphology of the wax precipitated from waxy crude oil in the presence of AMAC1.5 and PMAC1.5 during cooling is also researched. Figure 6 shows the microscopic photos of the waxy crude oil in the presence of AMAC1.5 at a concentration of 0.5 wt %. Unlike crude oil in absence of copolymers, wax crystals are not visible until the temperature is decreased to 58.5°C. In the present of PMAC1.5 at the same concentration, wax crystals are visible at the temperature of 58°C (Figure 7). Wax crystals keep growing into a larger size until the temperature decreases to around 55°C. Different from the crude oil in absence of copolymers, the crude oil in the presence of AMAC1.5 and PMAC1.5 contains smaller quantity

Table V. Fitting Parameters of the Viscosity-Temperature Curves Following the Arrhenius Equations for Crude Oil in the Absence and Presence of Copolymers

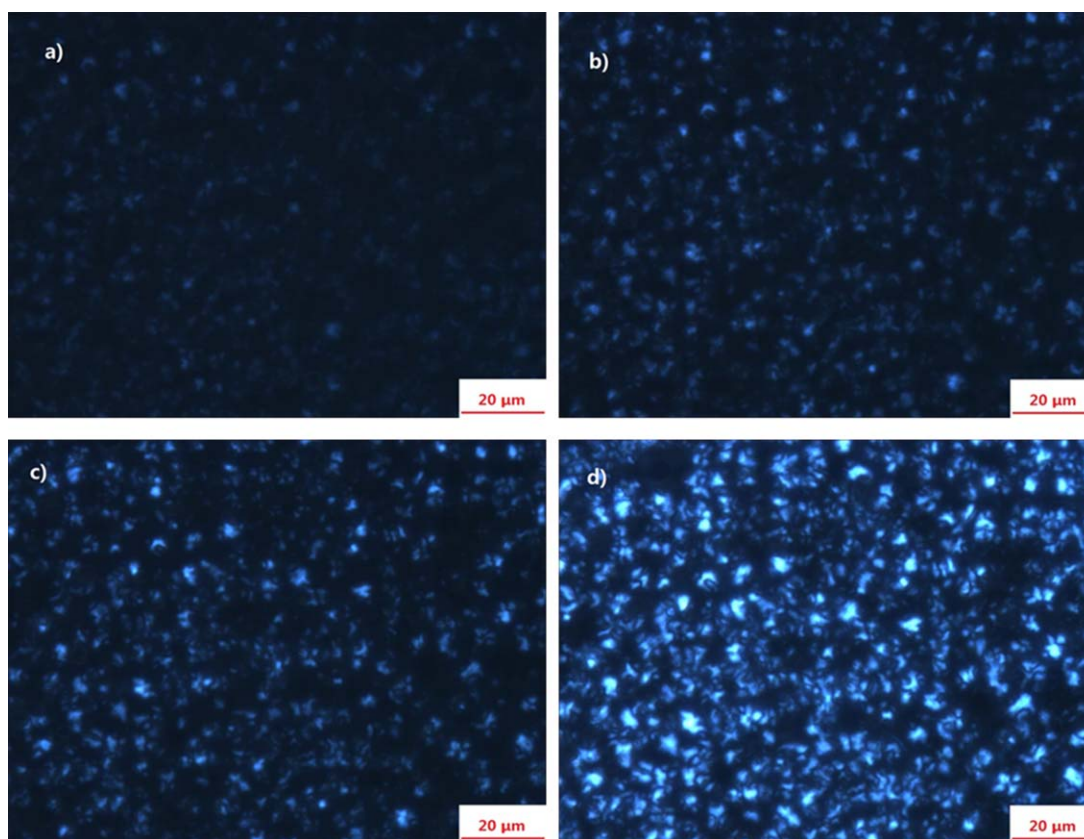|	WAT (K)	μ_0 (mPa s)	E_a/R (K)
Crude oil	332.0	75.6	13.3
0.5% MAC1.5	331.0	69.2	11.5
0.5% PMAC1.5	329.5	68.8	8.3
0.5% AMAC1.5	329.5	68.9	8.4

Figure 5. Polarizing light micrographs of crude oil in absence of copolymers during cooling: (a) 60°C; (b) 59°C; (c) 58°C; (d) 57°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and size of wax crystals at the similar temperatures. It is also found that the size of wax crystals in the presence of AMAC1.5 are smaller as compared with those in the presence of PMAC1.5, which indicates that AMAC1.5 is more efficient in dispersing the wax crystals in crude oil.

The WAT of crude oil in the absence of copolymer observed from the microscopic photos is 60°C, close to the WAT measured by rheological methods that is 59°C. In the presence of AMAC1.5 and PMAC1.5 at a concentration of 0.5 wt %, the WAT of crude oil observed from the microphotos are 58.5 and 58°C, which are 1.5–2°C higher than those measured by rheological methods. In general, the WAT determined from microscopic photos show good consistency with the previous rheological measurements.

From the previous rheological measurements, the non-Newtonian waxy crude oils in the presence of different copolymers show similar rheological behaviors. The transition from Newtonian to non-Newtonian behaviors for crude oil usually occurs at the temperature around 10–15°C below the WAT.[24] For this reason, 30°C is chosen as the measurement temperature, which is about 20°C below the WAT and ensures the oil samples being non-Newtonian fluids. At this temperature, the rheological curve of shear stress as a function of shear rate for crude oil in absence of copolymers is measured, and is shown in Figure 8. This curve is fitted following the Power Law, Bingham, and Casson model, respectively, which is expressed by eqs. (2)–(4).

$$\text{Power-Law model}: \tau = K\dot{\gamma}^n \tag{2}$$

where $\dot{\gamma}$ is the applied shear rate (s^{-1}), τ is the corresponding shear stress (Pa), K is the consistency index (Pa s), and n is the flow behavior index.

$$\text{Binham model}: \tau = \tau_0 + \eta\dot{\gamma} \tag{3}$$

$$\text{Casson model}: \tau = \left(\tau_0^{0.5} + (\dot{\gamma}\eta)^{0.5}\right)^2 \tag{4}$$

Where τ is the shear stress (Pa), τ_0 is the yield stress, η is the plastic viscosity (Pa s), and $\dot{\gamma}$ is the shear rate (s^{-1}).

Commonly, waxy crude oil, below the WAT, is considered to be pseudoplastic fluid, the viscosity of which decreases with the increase of shear rate.[24] The Power-Law model [eq. (2)] is often used to describe the flow behaviors of pseudoplastic fluid without yield stress. Binham model [eq. (3)] and Casson model [eq. (4)] are suitable for describing those fluids possessing a yield stress. In the case of fluids following the Bingham model, the relationship between shear stress and shear rate is linear. For those fluids following the Casson model, both yield stress and the nonlinear relationship between shear stress and shear rate should be considered.[25–27] From Figure 8, it is found that the Casson model fits the rhological data better than the other two. Moreover, the regression correlation coefficient (R^2) of Casson model is the highest among the three models, as shown in Table VI. In another word, the shear stress as a function of shear rate for Liaohe waxy crude oil in the absence of copolymers follows the Casson model better than the other two.
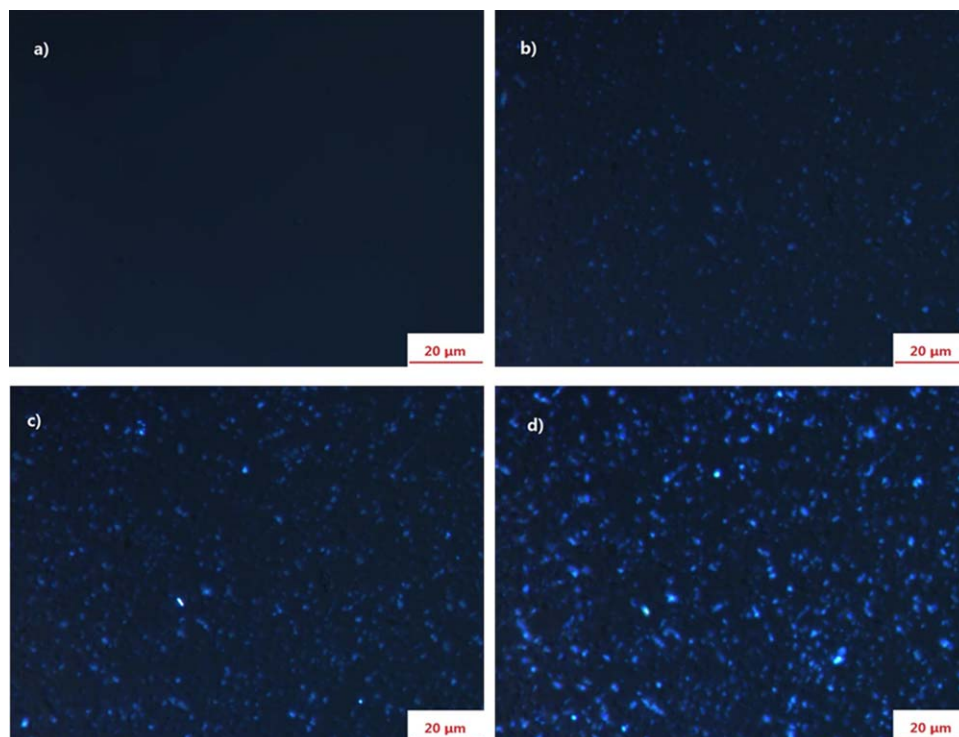
Figure 6. Polarizing light micrographs of crude oil in the presence of AMAC1.5 at the concentration of 0.5 wt % during cooling: (a) 60°C; (b) 58.5°C; (c) 57°C; (d) 55°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Efficiency of Copolymers on Improving the Flow Ability of Waxy Crude Oil

Casson model is a structural model, which is derived from the inner structure of fluids and often relates to the kinetic changes in these fluids. It has been proved to be useful for evaluating the rheological properties of food, such as chocolate and cocoa products.[28] Since the Casson model is supposed to express the relationship between the interior structural changes of fluid and
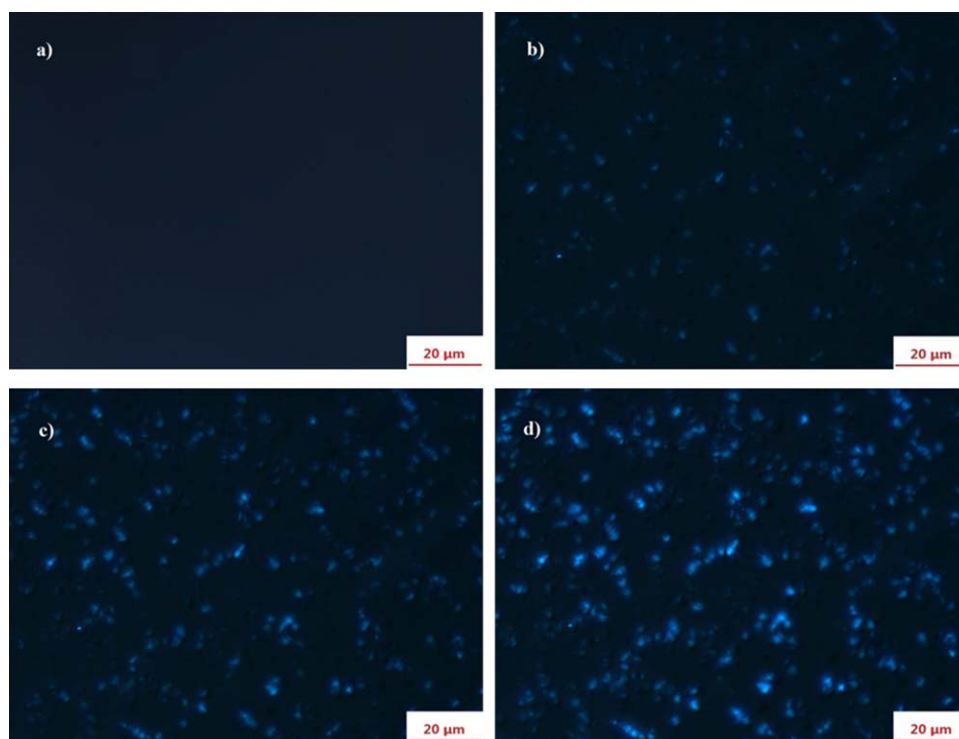

Figure 7. Polarizing light micrographs of crude oil in the presence of PMAC1.5 at the concentration of 0.5 wt % during cooling: (a) 60°C; (b) 58°C; (c) 57°C; (d) 55°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
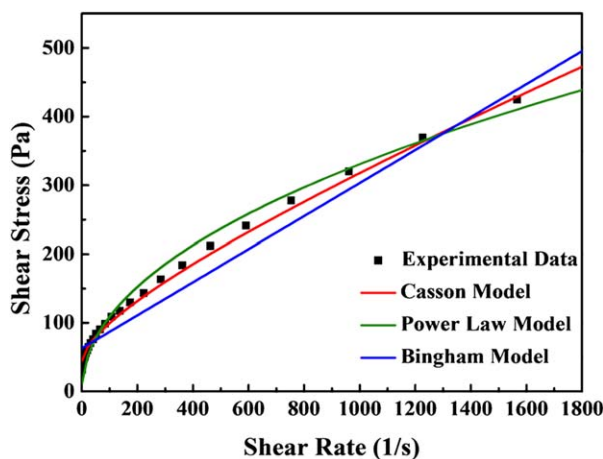
Figure 8. Fitting curves of the shear stress as a function of shear rate for Liaohe crude oil at 30°C following Casson, Power-Law, and Bingham model, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

apparent flow properties, it can be employed to demonstrate the effect of copolymers on the flow behaviors of waxy crude oil through the changes of fitting parameters.

In previous measurements, AMAC1.0 is found to have the best effect on reducing the yield stress of model oil. Thus, the effect of copolymer concentration on the rheological properties of crude oils is investigated by varying the concentration of AMAC1.0 from 0.1 to 0.7 wt %. The shear stress as a function of the shear rate is fitted following the Casson model, as shown in Figure 9. Below the concentration of 0.5 wt %, the shear stress decreases with the increase of copolymer concentration at the identical shear rate. However, the effect of copolymer on the reduction of the shear stress becomes worse as the concentration being increased to 0.7 wt %, close to the shear stress at the concentration of 0.3 wt %. Similar trend is also found for MAC and PMAC, the efficiency of which ceases to be improved at the concentrations higher than 0.5 wt %. It indicates that there is a limit to the effect of copolymer concentration on the reduction of shear stress.

The fitting parameters of shear stress as a function of shear rate are listed in Table VII. In this table, τ_0 is the calculated yield stress and η is the plastic viscosity, which refers to the slope of the flow curve at high shear rates. It is found that the Casson model well fits the rheological data supported by R^2, which are higher than 0.99. The fitted yield stress (τ_0) decreases with the increase of polymer concentration. To compare with the fitting parameters, the yield stress of crude oil in the presence of
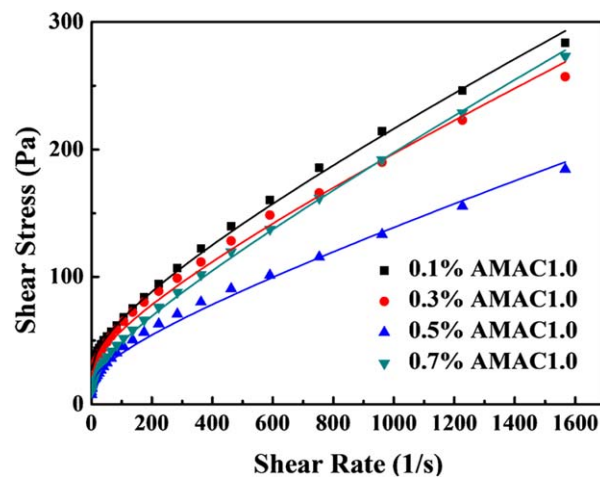

Figure 9. Fitting of the shear stress as a function of shear rate following the Casson model for waxy crude oil in the presence of AMAC1.0 at varying concentrations following the Casson model. The dotted lines are the rheological data, and the solid lines are the fitting curves following the Casson model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AMAC1.0 at different concentration is measured. Though the measured yield stress is lower than the calculated yield stress, the changes of them coincide with each other.

The effect of the grafting ratios of copolymers on the rheology of crude oils is investigated at the copolymer concentration of 0.5 wt %. The fitting of shear stress as a function of shear rate following the Casson model for crude oil in the presence of PMACs at the concentration of 0.5 wt % is shown in Figure 10, and that for crude oil in the presence of AMACs at the concentration of 0.5 wt % is shown in Figure 11. The calculated fitting parameters are listed in Table VIII. As shown in Figure 10 and Table VIII, the shear stress and fitted yield stress of crude oils in presence of PMAC1.0 are the lowest at the identical shear rate.

Similarly, as shown in Figure 11 and Table VIII, the shear stress and fitted yield stress of crude oils in the presence of AMAC 1.0 are the lowest. Table VIII shows that the plastic viscosity (η) of crude oil in the presence of PMACs decreases with the increase of grafting ratio, although the plastic viscosity in the presence of PMAC1.0 is very close to that in the presence of PMAC1.5. With the addition of AMACs, the plastic viscosity of crude oil

Table VI. Fitting Parameters Obtained from the Three Models

Power-law model	K	n	R^2
	11.9	0.481	0.985
Bingham model	τ_0	η	R^2
	62.9	0.240	0.956
Casson model	τ_0	η	R^2
	36.1	0.145	0.994

Table VII. Casson Fitting Parameters and the Measured Yield Stress for Crude Oils in the Presence of AMAC1.0 at Various Concentrations

Crude oil sample	τ_0	η	R^2	Yield stress (Pa)[a]
Oil + 0.1%AMAC1.0	26.2	0.092	0.999	21.5
Oil + 0.3%AMAC1.0	21.6	0.088	0.994	17.4
Oil + 0.5%AMAC1.0	14.5	0.064	0.993	10.7
Oil + 0.7%AMAC1.0	13.5	0.108	0.999	8.67

[a] The yield stress here is the experimental data measured by rheological methods.
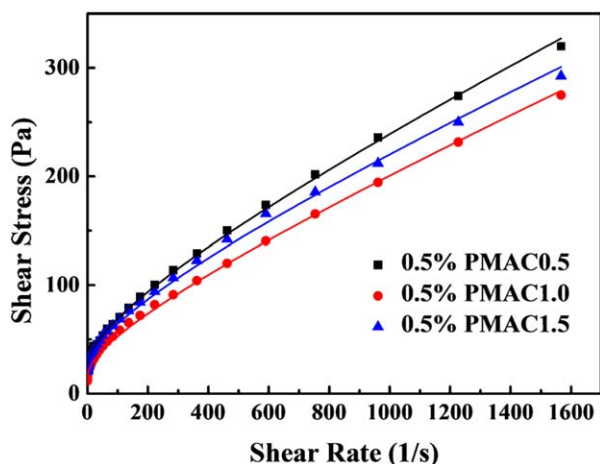
Figure 10. Fitting of the shear stress as a function of shear rate following the Casson model for waxy crude oil in the presence of PMACs at the concentration of 0.5 wt %. The dotted lines are the rheological data, and the solid lines are the fitting curves following the Casson model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Table VIII. Casson Fitting Parameters for Crude Oils in the Absence and Presence of Various Copolymers at the Concentration of 0.5 wt %

Sample	Grafting ratio	τ_0	η	R^2	Yield stress (Pa)[a]
Crude oil		36.2	0.145	0.994	40.3
Oil + 0.5%PMAC0.5	0.26	25.1	0.109	0.999	25.3
Oil + 0.5%PMAC1.0	0.68	16.7	0.102	0.998	13.4
Oil + 0.5%PMAC1.5	1.08	23.6	0.100	0.997	18.7
Oil + 0.5%AMAC0.5	0.31	17.2	0.085	0.999	16.1
Oil + 0.5%AMAC1.0	0.76	14.5	0.064	0.993	10.7
Oil + 0.5%AMAC1.5	0.98	16.4	0.077	0.992	13.8
Oil + 0.5%MAC1.5	1.10	29.5	0.097	0.991	24.7

[a] The yield stress here is the experimental data measured by rheological methods.

drops first and then increase with the increase of grafting ratio. The plastic viscosity in the presence of AMAC1.0 is the lowest. In general, PMAC1.0 and AMAC1.0, which possess a medium grafting ratio, have the best ability to reduce the fitted yield stress and the plastic viscosity. A high grafting ratio of copolymers does not mean the acquirement of a good flow of crude oil. The effect of the grafting ratio of AMACs and PMACs on the yield stress of crude oil is also examined (Table VIII), in which the measured yield stress has a similar change with the calculated one.

The effect of pendents on the rheology of crude oil is further discussed by comparing the fitting curves and parameters of MAC1.5, AMAC1.5, and PMAC1.5, which possess a close graft-
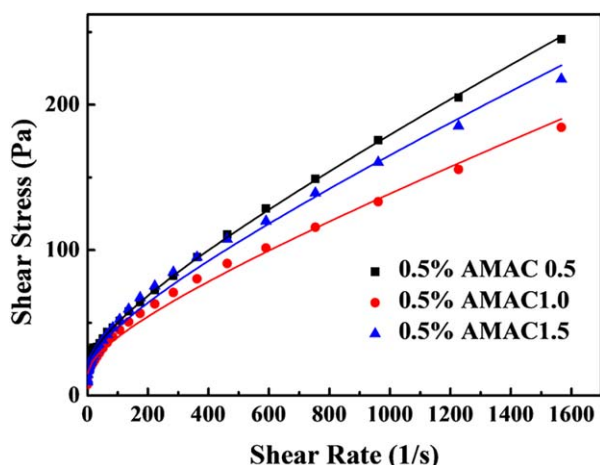
ing ratio at the concentration of 0.5 wt %, as shown in Figure 12 and Table VIII. The shear stress of crude oil in the presence of AMAC1.5 is the lowest among that of crude oil in the presence of three copolymers, next is in the presence of PMAC1.5. The shear stress in the presence of MAC1.5 is the highest. From Table VIII, it is also found that the Casson yield stress (τ_0) and plastic viscosity (η) of crude oils are decreased in the presence of AMAC1.5 and PMAC1.5, and parameters in the presence of AMAC1.5 is lower than that in the presence of PMAC1.5 at the same concentration. The Casson yield stress (τ_0) and plastic viscosity (η) of crude oils in the presence of MAC1.5 are the highest among that in the presence of the three copolymers. It indicates that phenyl pendants benefit for the copolymers improving the flow of crude oil better than PEG pendants and long alkyl pendants, which could be explained as: phenyl groups enable AMAC to have a better interaction with the AS, owing to their aromatic structure, and hinder the AS from forming
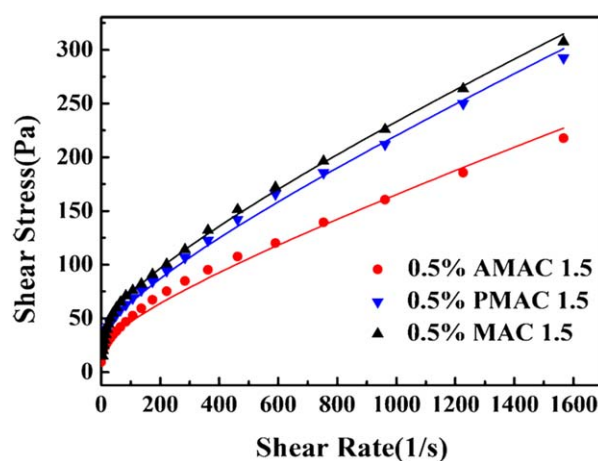

Figure 11. Fitting of the shear stress as a function of shear rate following the Casson model for waxy crude oil in the presence of AMACs at the concentration of 0.5 wt %. The dotted lines are the rheological data, and the solid lines are the fitting curves following the Casson model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 12. Comparison of the fitting of shear stress as a function of shear rate following the Casson model for waxy crude oil in the presence of MAC1.5, AMAC1.5, and PMAC1.5 at the concentration of 0.5 wt %. The dotted lines are the rheological data, and the solid lines are the fitting curves following the Casson model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

large aggregates. The yield stress of crude oil in presence of PMAC1.5, AMAC1.5, and MAC1.5 at the concentration of 0.5 wt % and 30°C is also measured, as shown in Table VIII. Among the three copolymers, AMAC1.5 is still the most effective for reducing the yield stress of crude oil. PMAC1.5 performs better than MAC1.5, although not as good as AMAC1.5, indicating that polar oxyethyl groups may be more efficient than alkyl pendants in impairing the aggregating of the AS in crude oil at low temperature by a stronger interaction with the AS. The consistency between the measured and calculated yield stress indicates that Casson model is valid and accurate for predicting the rheological behaviors of waxy crude oil.

CONCLUSIONS

Comb-type PMAC and AMAC copolymers with various grafting ratios (R_g), which are the ratios of PEG or aniline to maleic anhydride group, are successfully synthesized by free-radical copolymerization. The chemical structure of these copolymers is confirmed by ^{1}H NMR spectra, and R_g of copolymers is calculated by integrating the peak area of protons in ^{1}H NMR spectra. WAT of Liaohe crude oil in the absence and presence of copolymer is characterized by fitting the original data of viscosity as a function of temperature following the Arrhenius Equation, which is also identified by the microscopic observations. The results show that these copolymers obviously reduce the WAT of crude oil and decrease the size of wax crystals. The rheological curve of shear stress as a function of shear rate is fitted following the Power Law, Bingham, and Casson model, respectively. Casson model is found to fit the curve better than the others and then is applied to fit the curves of crude oil in presence of different copolymers. The fitting and experimental results indicate that the sequence of copolymers reducing the yield stress of crude oil at the similar concentration and grafting ratio is AMAC > PMAC > MAC. Especially, crude oil in the presence of AMAC1.0 at the concentration of 0.5 wt % shows the lowest yield stress among all of the tested oil samples. A high R_g or concentration of copolymer does not equal to a good flow ability of crude oil. As a result, Casson model is an appropriate model for simulating the rheological behaviors of waxy crude oil.

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