HOW COMB-TYPE POLY(MALEIC ACID ALKYLAMIDE -CO-α-OLEFIN) ASSEMBLES IN WAXY OILS AND IMPROVES COLD FLOWING ABILITY

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Introduction

Crude oils are complex hydrocarbon mixtures containing nonpolar paraffins and polar components, such as asphaltenes. At high temperature, crude oils behave as Newtonian fluids with low viscosities [1]. But at low temperature, the solubility of long chain n-paraffins and asphaltenes decreases sharply. In oil industry, the deposition of long chain n-paraffins and asphaltenes on the pipe wall can result in reducing oil flow and even blocking the pipeline. To solve this problem, thermal, mechanical (pigging) and chemical (wax inhibitor) methods are available, and the comb-type polymer additives are important chemical inhibitors. Polymers with crystalline /amorphous diblock structures such as ethylene-vinyl acetate copolymer [2], polyethylene-poly(ethylenepropylene) [3], poly (ethylene-butene) (PEB) [4-5], and comb-type poly(maleic anhydride-co-α-olefin)s esterified by alkyl alcohols [6] have been reported as wax inhibitors for waxy oils [7].

In this paper, we reported the synthesis of novel comb-type polymers based on poly (maleic alkylamide -co-α-olefin) (MAC) with different length of side chains. Their effects on the rheological properties of waxy oils and the crystallization of long chain n-paraffins upon cooling were examined by means of rheology, DSC and optical microscopy.

Experimental

Materials. Decane (anhydrous, 99+%), hexatriacontane (C36, >98%,), maleic anhydride (99%), α-octadecene (95%), α-dodecene (95%), benzoyl peroxide (99%), o-xylene (98%), octadecylamine (97%) and dodecylamine (98%) were purchased from Acros company and were used as obtained.

Model waxy oil samples were prepared by dissolving hexatriacontane (C36) in decane. The crude oil used in this work containing 15.5 wt% paraffins and 0.6 wt% asphaltenes were obtained from Changqing oil field.

Synthesis of MAC. Poly(maleic alkylamide-co-α-olefin) (MAC) was synthesized from alfa-olefins with long n-alkene side chain and maleic anhydride (**Fig. 1a**). By amidation with excess (**Fig. 1b**) long chain n-amines, the comb-type poly(maleic alkylamide-co-α-olefin)s were obtained. In this paper, three polymers MAC18-18 (from α-octadecene and octadecylamine), MAC12-18 (from α-dodecene and octadecylamine) and MAC12-12 (from α-dodecene and dodecylamine) were used.

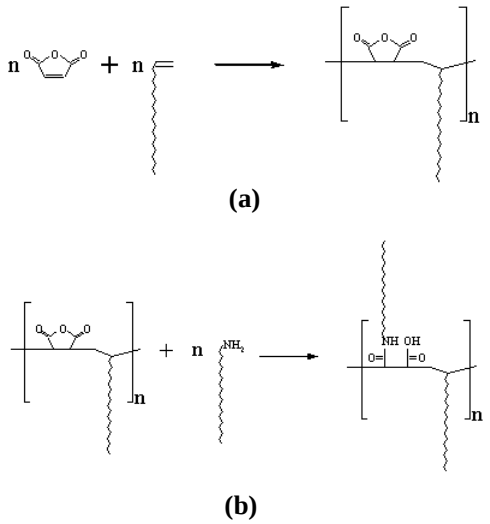


Figure 1. Synthesis of (a) poly(α-olefin-co-maleic anhydride) and (b) poly(α-olefin-co-maleic anhydride amide) (MAC) with the amidation ratio f = 1.

The molecular weights and molecular weight distributions were determined by GPC using poly(styrene) samples as standards. The molecular weight and molecular weight distribution of MAC18-18 were 11.2 kg/mol and 1.5, respectively.

Yield Stress Measurement. The yield stress (τ_y) is defined as the stress below which no flow occurs. An operational definition of τ_y is adopted as the stress at the transition between the creep and liquid-like viscosity regimes where τ_y can be identified as the stress for which the derivative is a maximum. The yield stress measurements were performed on a Physica MCR101 controlled stress rheometer with a 50 mm copper parallel plate. Oil samples were heated to 70 °C, kept at this temperature for 5 minutes to erase their thermal history and then cooled to the experimental test temperature at a rate of ca. 10 °C/min. With both the waxy oils and crude oil stress tests were made at 0^oC. After allowing samples to anneal at constant temperature under no stress for 5 minutes, stress was applied and incrementally increased every 10 seconds (100 stress increments per decade) and the viscosity was measured. The initial applied stress was chosen well below the stress at which creep beginned.

Polarized Optical Microscopy. Wax crystal morphologies were observed using an Olympus BX51 Polarized optical microscope with a Linkam THMS 600 hot stage. Images were captured using an Olympus DP70 camera connected to a PC via a PIXCID imaging board. A small quantity of model waxy oil was transferred from storage at room temperature directly to a glass slide inside a copper stage with a central window for observation. Images were taken at five sites on the slides.

Differential Scanning Calorimetry (DSC). The differential scanning calorimeter is a Perkin-Elmer (Norwalk, CT) Pyris DSC 7. The temperature scale was calibrated by the melting temperature of ice from DI water and the heat flow by the fusion of an indium standard. An empty stainless steel sample pan was used as the reference and the baseline was established by running an empty pan before the sample measurement. About 10 mg model waxy oil was weighed into a pan, hermetically sealed, and then placed in the DSC sample tray. Scanning rates ranged from 1 to 10 ° C/min, and the temperature ranges were chosen to ensure that the base line was stable for at least ten degrees before the first peak and after the last peak. The calorimeter chamber was continuously purged with dry nitrogen. The enthalpies of crystallization and melting of paraffins were calculated from the peak areas using the Pyris software. Regular sampling showed no weight loss from the hermetically sealed sample pans.

Results and Discussion

Effect on rheology for model waxy oil. **Fig. 2** shows that the yield stresses of the gels of model waxy oil (4%C36 solutions in decane) formed upon cooling to 0°C were reduced by addition of 0.1 wt% MAC18-18, MAC12-18 and MAC12-12, and MAC18-18 is the most effective one among them. Their efficiency on reducing τ_y has a sequence of MAC18-18 > MAC12-18 ≈ MAC12-12.

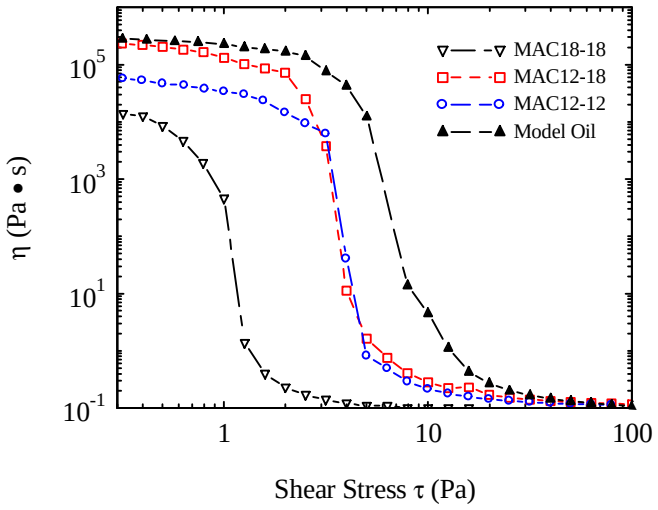


Figure 2. Effect of MAC18-18, MAC12-18 and MAC12-12 on the yield stresses of model waxy oils (4%C36).

Table1 The yield stresses of 4% C36 and 4%C36 +0.1% MACs

Samples	Yield stress τ_y (Pa)	Relative yield stress
Model waxy oil(4%C36)	7.5	1
4%C36+0.1%MAC18-18	1.2	0.16
4%C36+0.1%MAC12-18	2.7	0.36
4%C36+0.1%MAC12-12	3.0	0.40

Effect on rheology for crude oil. As shown in **Fig. 3**, MAC18-18 is also the most effective one in improving the cold flowing ability for crude oil. The efficiency on reducing τ_y shows the sequence of MAC18-18>MAC12-18>MAC12-12.

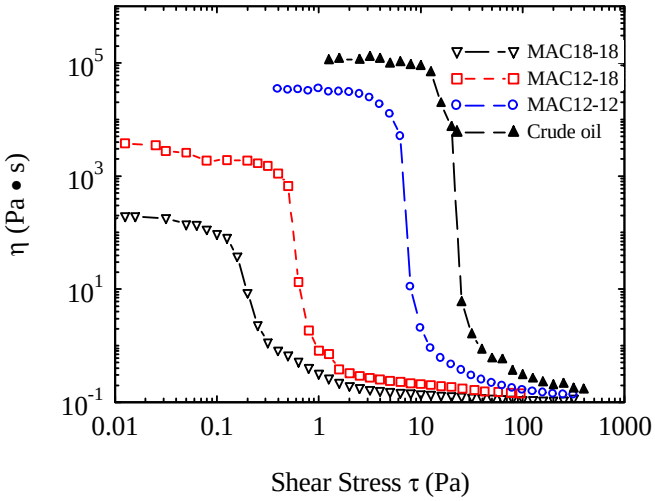


Figure 3. Effect of MAC18-18, MAC12-18 and MAC12-12 on the yield stresses of crude oils.

Table 2 The yield stresses of crude oils and crude oils+0.1%MACs

Samples	Yield stress τ_y (Pa)	Relative yield stress
Crude oils	11.6	1
Crude oils +0.1%MAC18-18	0.1	0.009
Crude oils +0.1%MAC12-18	0.6	0.05
Crude oils +0.1%MAC12-12	7.2	0.6

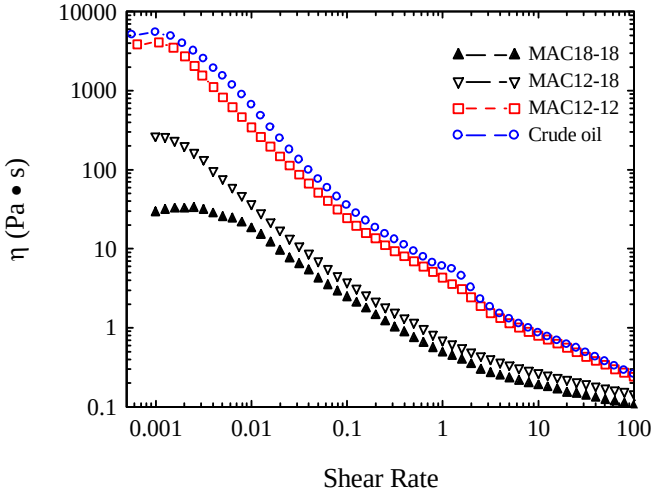
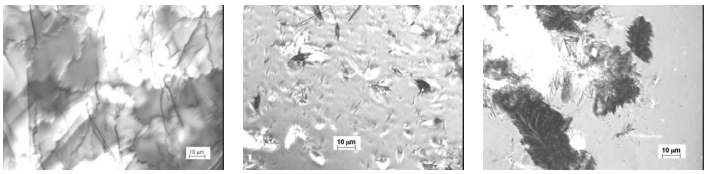


Figure 4. Effect of MAC18-18, MAC12-18 and MAC12-12 on the viscosities of crude oils.

Fig. 4 indicates MACs can reduce the viscosities of crude oils with the sequence of MAC18-18>MAC12-18>MAC12-12.

Compared with model waxy oils, MACs can reduce the yield stresses of crude oils more significantly, for example, MAC18-18 can reduce τ_y by two orders of magnitude. This may due to the carboxyl and amide groups in MAC interact with asphaltenes in crude oils which model waxy oils do not contain.

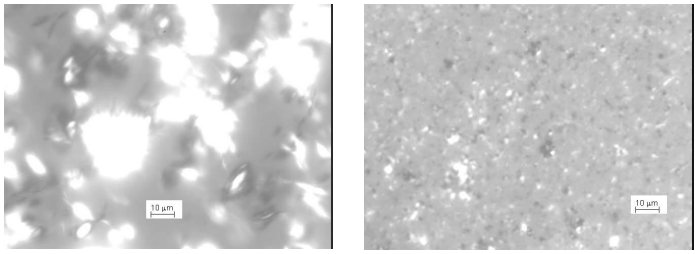
Effect on crystal morphology. As observed by polarized optical microscopy (**Fig. 5**), the size of C36 crystals from 4 wt% solutions in decane at 0 °C was reduced by MAC18-18 significantly. The shape changed from large plate-like crystals to irregular particles. However, comparing two samples with different addition amount of MAC18-18 **(Fig. 5b and c**), the size of C36 crystals with 0.05% MAC18-18 is smaller than that with 0.1% MAC18-18. The extra polymer chains may have "bridging effect" to connect C36 crystals which is unfavorable to flowing ability.



(a) (b) (c)

Figure 5. Polarized optical micrographs of crystals from (a) 4 wt% C36, (b) 4 wt% C36 + 0.05% MAC18-18, and (c) 4 wt% C36 + 0.1% MAC18-18.

Crude oil samples with and without MACs were also observed by polarized optical microscope **(Fig. 6)**. Up addition of 0.1%MAC18-18, both the paraffin crystals and the asphaltenes (black particles in the figure) become much smaller than those without MAC.



(a) (b)

Figure 6. Optical micrographs of (a) crude oil and (b) crude oil + 0.1%MAC18-18.

Effect on crystallization of model waxy oil. Further insight on the influence of MAC on paraffin crystallization from the model waxy oil is observed from DSC (**Fig. 7**). Addition of MACs broadens the phase transition peaks upon cooling and moves the onset of paraffin crystallization to slightly lower temperatures with a parallel trend to lower enthalpies of the transitions. These effects follow the sequence MAC18-18 > MAC12-18 > MAC12-12 at 0.1% polymer concentration. These trends in onset temperature and crystallization enthalpy are accentuated as the concentration of MAC18-18 is increased **(Fig. 7)**.

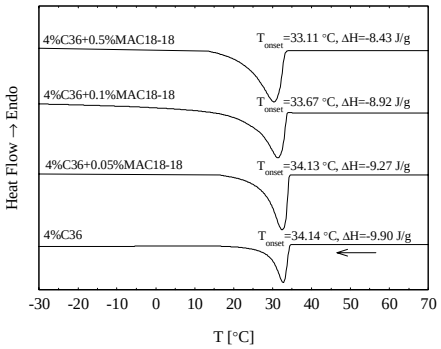


Figure 7. DSC thermographs of crystals from 4 wt% C36 in decane with addition of several concentrations of MAC18-18 during cooling at 10 °C/min.

Conclusion

We reported the synthesis of comb-type polymers (MAC) based on the amidation of poly(α-olefin-co-maleic anhydride) by alkyl amines. These copolymers reduced significantly the yield stresses of the model waxy oils and crude oils, and decreased the size of long chain n-paraffin crystals and asphaltene aggregations upon cooling. The MACs either self-assemble to induce the crystallization of long chain n-paraffins, or co-crystallize with them by the non-polar side chains and thus inhibit the growth of paraffin crystals by the layer of the polar parts, while the carboxyl and amide groups interact with polar asphaltenes to alleviate their aggregation upon cooling. The effect of MAC on flowing ability improvement for waxy oil is related to the side-chain length. In our experiments, the longer the side-chain is, the better is the result (MAC18-18>MAC12-18>MAC12-12).

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