Improvement of flow ability of oils by Poly(maleic acid alkylamide-co-α-olefin-co-styrene)

Jun Xu, Jingjing Xu, Shili Xing, Xuhong Guo*

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.
(corresponding author: Guoxuhong@ecust.edu.cn)*

In petroleum industry, the precipitation of long chain paraffins and asphaltenes can lead to waxy deposition at the pipe walls, reducing oil flow and potentially blocking the pipeline. The problem becomes more serious for offshore deep-sea wells where the temperature at the sea bed can be 4 ℃ or lower. To improve the flow ability of crude oil, heating and mechanical pigging have been tried [4]. But these methods consume too much energy and are uneconomic. Using the chemical additives to alleviate or solve the wax deposition problem becomes a better choice and an important method which has absorbed intensive research interests. Several kinds of comb-type polymer additives such as poly(ethylene-butene) (PEB) and poly(maleic anhydride-co-α-olefin) (MAC) have been reported to be effective to improve the cold flow ability of waxy oils [5-8].

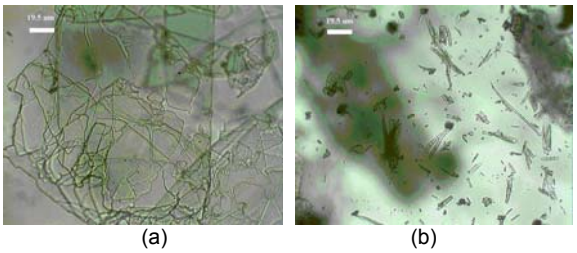
In this work, with α-octadecene, maleic anhydride and styrene, new comb-type copolymers of poly(maleic acid alkylamide-co-α-olefin-co-styrene) (MASC) with different ratios of styrene to maleic anhydride (MA) were synthesized by free-radical polymerization. Three kinds of synthesized terpolymer were named individually MASC0.5, MASC0.75 and MASC1.0 for their feeding ratio of styrene to MA being 0.5, 0.75 and 1.0.

The chemical structure of terpolymers was confirmed by FT-IR and ^{1}H NMR spectroscopy. In the FT-IR spectra, adsorption at 1720 cm^{-1} is the stretching of the carbonyl group (C=O) from maleic anhydride unit. Two adsorptions separately at 1613 cm^{-1} and 705 cm^{-1} are the characteristic absorptions from the styrene. In the ^{1}H NMR spectrum, peaks found at 7.2ppm, 3.5ppm, and 0.89ppm were protons in phenyl group (-C_6H_5) of styrene unit, in –CH–CH– of maleic anhydride unit and in -CH_3 of octadecene unit, respectively. In addition, the molecular weight of MASC0.5, MASC0.75 and MASC1.0 was 16.9, 24.4, 21.9 kg/mol, determined by GPC with THF as solvent.

The yield stress measurements were performed on a Physica MCR101 controlled stress rheometer with a 25 mm parallel plate. The yield stress (τ_y) is defined as the stress below which no flow occurs. An operational definition of the yield stress is adopted as the stress at the transition between the creep and liquid-like viscosity regimes where the yield stress can be identified as the stress for which the derivative is a maximum [2]. The initial applied stress was chosen well below the stress at which creep began.

In order to explore the interactions between paraffins and terpolymer, model oil was prepared by dissolving 4% (weight) hexatriacontane (C36) in decane. It is found that the yield stress of the model waxy oil decreased with variation of the concentration of MASCs from 0% to 0.05% and 0.05% to 0.10% (weight). However, higher concentration of 0.20% can not continue to reduce the yield stress of model waxy oil. Obviously, 0.10% of concentration is the best for reduction of yield stress of model oil.

With the addition of 0.10% MASCs, the crystal of model oil became smaller and the shapes changed significantly from large plate-like crystals to small plates or spindle shape of indistinct geometry (Fig. 1). In Fig.1, MASC0.75 shows the best effect on the morphology and distribution of paraffin crystals which is identical to the rheological results.



(a) (b)

Fig. 1. Optical micrographs of crystals from 4 wt% hexatriacontane (C36). (a) C36; (b) C36 +0.10% MASC0.75.

As above shows, novel comb-type Poly(maleic acid alkylamide-co-α-olefin-co-styrene)s (MASCs) were synthesized successfully by free-radical copolymerization. The rheological and microscopic tests indicate that MASCs can significantly reduce the yield stress and decrease the crystal size of model waxy oil at low temperature. In fact, they possess great potential to improve the cold flow ability of crude oil.

References

[1] Xuhong Guo, Robert K. Prud'homme, et al. (2004) Macromolecules. 37, 5628-5645.
[2] Probjot Singh, H. Scott Fogler, et al. (2001) Fluid Mechanics and Transport Phenomena. 47, 6-18.