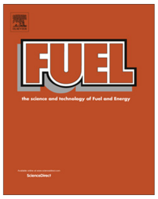
Fuel 203 (2017) 570–578

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Full Length Article

The yield stress of model waxy oil after incorporation of organic montmorillonite

Chong Gao [a], Cunzhe He [a,b], Yanfen Ding [b], Juan Chen [b], Feng Wang [b], Peng Liu [b], Shimin Zhang [b], Zengxi Li [a], Mingshu Yang [a,b,*]

[a] *School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, 19 A Yuquan Rd, Shijingshan District, Beijing 100049, PR China*

[b] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun North First Street 2, Beijing 100190, PR China*

HIGHLIGHTS

- The organic montmorillonite (OMMT) decreased the yield stress of model waxy oil.
- The OMMT decreased the crystallinity and the dimension of the wax crystals.
- The OMMT inhibited gelation of the wax crystals.
- The OMMT changed the dependence of yield stress on thermal history.

ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form 28 April 2017
Accepted 3 May 2017

Keywords:
Organic montmorillonite
Model waxy oil
Yield stress
Thermal history

ABSTRACT

To study the influence of organic montmorillonite (OMMT) on the yield stress of the model waxy oil (LMO) under dynamic cooling, OMMT was prepared through ion exchange of the sodium montmorillonite with dimethyldioctadecylammonium chloride (DOAC). The incorporation of OMMT lead to a great reduction of the yield stress, which could be explained by the inhibition effect of OMMT on the wax gelation. For 100 ppm OMMT loading, the yield stress reduced by 74.1% at 36 °C. The inhibition effect was realized through decreasing the wax crystallinity, reducing the crystal dimension and introducing the electrostatic repulsion between the crystal particles. The role of thermal history on the yield stress was also studied. Compared with the pure LMO, the OMMT-doped LMO showed different dependence level on the thermal history, but similar trend with that. High testing temperature and short holding time facilitated a lower yield stress. Due to the presence of different shear stress during cooling, the cooling rate showed a complicated effect on the yielding process.

1. Introduction

When the waxy crude oil is cooled to temperatures below the wax appearance temperature (WAT), the paraffin molecules in the oil would begin to precipitate and crystallize. Due to the large aspect ratio, the precipitated wax crystal particles can form interlocked networks at a precipitation amount as low as ~1.0 wt% [1]. That is to say, the wax gelation is conducted. With evolution of the wax gelation, the crude oil behaves like a solid-like fluid and even finally stops flowing. When the crude oil is transported through pipelines, an inlet gauge pressure is needed to destroy the wax gel and restart the flow. Based on the wax gel deformation rheology and the Navier-Stokes theory, the restart pressure can be predicted, which is related to the dimension of pipes, the compressibility and especially the yield stress of the waxy oil [2–7]. To minimize the operation risk, the pressure as small as possible is required, which can be achieved through controlling the yield stress.

To modulate the yield stress, the most well-known method is to pretreat the waxy crude oil with polymeric pour point depressants (PPDs). The depressants possess high interface activity, which can contribute to controlling the morphology of wax crystals and the interaction between them [8]. To date, various of polymers have been developed and employed, most of which are linear or comb-like olefin copolymers and acrylate copolymers, such as poly(ethylene-co-vinyl acetate) (EVA), poly(styrene-co-octadecyl maleimide), poly(octadecyl acrylate-co-acrylic acid), and so on

---

* Corresponding author at: Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun North First Street 2, Beijing 100190, PR China.

E-mail address: yms@iccas.ac.cn (M. Yang).

http://dx.doi.org/10.1016/j.fuel.2017.05.011

[9–14]. Depending on the molecular weight and components of PPD, as well as the oil composition, the yield stress decrement ranges from dozens of percent to several orders of magnitude [9–14]. Recently, some nanoparticles have been introduced into the conventional depressants, exhibiting enhanced effects on yield stress reducing and flow improving. An EVA/organic montmorillonite (OMMT) nano-hybrid material was prepared and it significantly decreased the pour point and viscosity of Daqing crude oil [15–16]. Through controlling the wax crystal morphology and the intercrystal electrostatic interaction, the EVA/OMMT nano-hybrid depressant exhibited more excellent performance on reducing the yield stress than the commercial depressant N6 [16]. The yield stress of Daqing crude oil at 22 °C was found to decrease by 99.3% from 273.30 Pa to 1.97 Pa [16]. Yang et al. reported that the yield stress of Changqing oil could also be reduced by 85.5% with a dosage of 50 ppm EVA/OMMT [17]. Similar to EVA/OMMT, poly(octadecyl acrylate) (POA)/OMMT nano-hybrid (weight ratio 1:1) also decreased the yield stress of Changqing oil, comparable to the POA alone [18]. Nanosilica was also incorporated into POA to prepare the nano-hybrid depressant, which was able to decrease the yield stress of model waxy oil at 18 °C from ~100 Pa to 0.2 Pa, in comparison with 1.0 Pa for the neat POA [8]. These nano-hybrid materials can reduce polymer usage and may be potential substitutes for commercial polymer additives in the future.

The thermal history, including cooling rate, testing temperature and holding time, also makes impacts on the yield stress [19–25]. As to the effect of cooling rate, most of the recent reports agreed that a rapid cooling produced smaller wax crystal particles, then weaker networks and smaller yield stress thereof [20–23]. However, the earlier report from Russell in 1971 found that a rapid cooling resulted in stronger networks [19]. Testing temperature controls the solubility of paraffin molecules in the solvent. Lower temperature yields higher precipitation, then stronger wax networks and finally greater yield stress [21,23]. Regarding to the influence of holding time, conflicting results were obtained in previous studies. In many cases, with holding time increasing, stronger wax networks were built, leading to a rising trend of the yield stress [24–25]. In contrary, Chang reported that the holding time had insignificant effects on the yield stress, and the disagreement was explained by different oil composition [23]. As well as thermal history, the shear condition, including the shear stress and the shear rate, influences greatly on the morphology and gelation of wax crystals [20,26]. Venkatesan found that a maximum yield stress was obtained with increasing the shear stress (0–5 Pa) or the shear rate (0–10 s^{-1}) [20] This was well explained by the competing effects: facilitating and inhibiting the wax gelation at different values of shear stress and rate, respectively [20]. However, the monotonous decreasing trend of the wax gel strength with the shear rate was found by Kane, which might be because of the different oil composition and the applied large shear rates (10 and 500 s^{-1}) [26].

Polymer/OMMT nano-hybrid depressants have been investigated and used in real oil transportation in China for yield stress reducing and flow improving [15–18]. However, the effect of OMMT as a single-component additive has not been studied. The action mechanism of OMMT is not clearly understood, which would be extremely important to design and formulate effective additives for oil transportation. In this work, OMMT, prepared by modifying montmorillonite with long-chain quaternary ammonium surfactants, was used as a unique additive in the model waxy oil. The influence of OMMT on the yield stress of the model waxy oil was studied. To clarify the action mechanism, the evolution of wax crystals was monitored. According to the experimental results, a possible mechanism of OMMT was proposed. Besides, the yield stress dependence on thermal history was also analyzed.

2. Experimental

2.1. Materials

Sodium montmorillonite clay (MMT) was purchased from Zhangjiakou Qinghe Chemical Factory (Hebei, China). Dimethyldioctadecylammonium chloride [$(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$, denoted as DOAC], was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Toluene (analytical reagent) was purchased from Beijing Chemical Works (Beijing, China). Solid paraffin (wax) was provided by SINOPEC Beijing Yanshan Petrochemical Company. Liquid paraffin (chemically pure) was purchased from Xilong Chemical Co., Ltd. (Guangzhou, China).

2.2. Preparation and characterization of OMMT

The OMMT was prepared by the so-called cation-exchange reaction of MMT with DOAC according to the method reported by Qin et al. [27]. The Fourier transform infrared (FTIR) spectra of the organic clay in the wavenumber range of 4000–400 cm^{-1} were obtained on a Nicolet Avatar 6700 FTIR spectrometer equipped with an attenuated total reflectance device (Thermal Fisher Scientific Inc. America). The X-ray diffraction (XRD) patterns of the MMT and OMMT were measured by a high-power Rigaku XRD instrument (D/max 2500, Japan) with Cu-Kα radiation ($\lambda = 0.154$ nm, 40 kV, 120 mA) at 25 °C. The diffractograms were scanned from 2° to 40° (2θ) at a scanning rate of 4°/min. To measure the organic content in OMMT, thermogravimetric analysis (TGA) was performed on a Pyris 1 apparatus (PerkinElmer Inc. America) under nitrogen atmosphere at a flow rate of 25 mL/min from 100 to 700 °C at a heating rate of 20 °C/min.

2.3. Preparation of the model waxy oil

The model waxy oil containing 20.0 wt% wax was prepared by dissolving 10 g of wax in 40 g of liquid paraffin at 65 °C. The carbon number distribution of the wax was determined using a high-resolution dual-focus magnetic mass spectrometer (DFS, Thermo Fisher Scientific) and is provided in Fig. 1. The average carbon number $\bar{n}$ of the model waxy oil was 30.3, which was calculated using the equation in the Refs. [28–30].

2.4. Preparation of the doped oils

Here, OMMT dispersions were prepared in toluene under stirring for 30 min at different concentrations. The model waxy oil

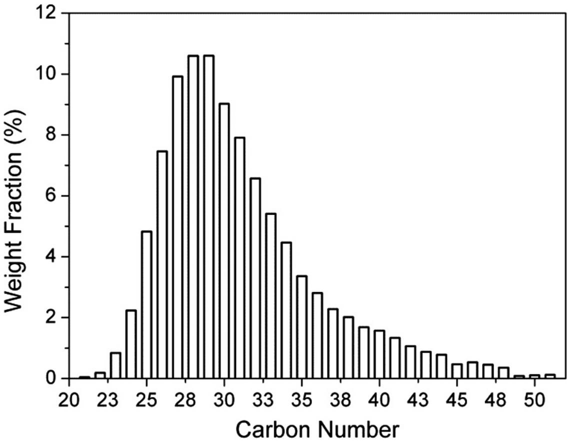


Fig. 1. Carbon number distribution of the wax.