Fuel 207 (2017) 204–213

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Performance improvement of the ethylene-vinyl acetate copolymer (EVA) pour point depressant by small dosages of the polymethylsilsesquioxane (PMSQ) microsphere: An experimental study

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HIGHLIGHTS

- Small dosages of the PMSQ microsphere (≤10 ppm) improve the performance of EVA PPD.
- The best dosage of the PMSQ microsphere is found to be around 2.5 ppm.
- The EVA molecules can adsorb and concentrate on the PMSQ microsphere.
- The formed EVA/PMSQ composite particles can act as the nucleation template for wax precipitation.
- The formed composite particles greatly modify the precipitated wax crystals' morphology.

ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form 19 June 2017
Accepted 20 June 2017
Available online 26 June 2017

Keywords:
Waxy crude oil
EVA
PMSQ microsphere
Flow behavior
Performance improvement

ABSTRACT

In a previous work, the addition of the polymethylsilsesquioxane (PMSQ) microsphere (50–400 ppm) can improve the flow behavior of waxy crude oil through the spacial hindrance effect. However, the flow improving efficiency of the neat PMSQ microsphere is not as good as the traditional polymeric pour point depressants (PPDs). In this paper, the effect of the ethylene-vinyl acetate copolymer (EVA2806) PPD together with the PMSQ microsphere (with the size around 2 μm) on the flow behavior of a typical waxy crude oil was investigated. The results show that adding 50 ppm EVA PPD can greatly improve the flow behavior of the oil. The neat PMSQ microsphere cannot improve the flow behavior of the oil at small dosages (≤10 ppm), but can significantly improve the performance of the EVA PPD. The gelation point, G′, G″, transient apparent viscosity and yield stress of the oil decrease further after adding both 50 ppm EVA and a small amount of the PMSQ microsphere (≤10 ppm). The best flow improving efficiency is found at 50 ppm EVA + 2.5 ppm PMSQ. The addition of the PMSQ microsphere has little influence on the WAT and precipitated wax crystal amount of the oil doped with EVA, but outstandingly changes the morphology of the precipitated wax crystals into larger and more compact flocs. The adsorption tests show that the EVA molecules can adsorb and concentrate on the PMSQ microsphere, thus causing the formation of the EVA/PMSQ composite particles. The composite particles can act as nucleation templates for the wax precipitation, resulting in larger and more compact wax microstructures and then further improving the flow behavior of the oil. The PMSQ microsphere dosage and the amount of EVA PPD adsorbed on the microsphere obviously influence the performance of the composite particle with the best performance at 50 ppm EVA + 2.5 ppm PMSQ. The findings mentioned above provide a new way to improve the performance of polymeric PPDs efficiently.

1. Introduction

The precipitation of paraffin waxes brings huge challenges to the production and pipeline transportation of waxy crude oil. When the temperature of waxy crude oil is below its wax appearance temperature (WAT), paraffin waxes start to precipitate from the oil due to super-saturation [1]. The precipitated wax crystals are normally irregular (plate-like or needle-like) and are liable to form a continuous three dimensional network at relatively low wax crystal concentrations (around 1 wt%) [2,3]. The formed wax

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http://dx.doi.org/10.1016/j.fuel.2017.06.083
0016-2361/

crystal network structure occludes large amounts of liquid oil and then seriously aggravates the rheology of waxy crude oil, which makes the pipeline transportation of waxy crude oil more difficult and dangerous [4,5].

Polymeric pour point depressants (PPDs) are often added into waxy crude oil to improve the rheology of the oil, thus ensuring the safe and economic transportation of the oil in pipelines [6]. The molecular structure of polymeric PPDs normally contains both the non-polar long alkyl chains (≥C18) and the polar groups. The long alkyl chains, which could be located either in the backbone or in the side chain of PPD molecules, can take part in the precipitation process of paraffin waxes through nucleation, adsorption and co-crystallization effects. The polar groups such as the ester group, maleic anhydride group, and vinyl acetate (VA) group, could control the dispersion state of PPD molecules in oil phase and interfere the growth of wax crystals [7,8]. Ethylene-vinyl acetate copolymer (EVA) is a kind of effective polymeric PPDs and has been widely used in pipelines transporting waxy crude oil [6,9–12]. The polyethylene group of EVA belongs to the long alkyl chains, while the VA group of EVA is a polar group. Much work has been done on the mechanism and performance EVA PPD so as to guide the application of EVA PPD better [6,9–12]. The results showed that the EVA PPD favors the formation of island defects on the wax crystals surface and weakens the interactions between the precipitated wax crystals [6,10,12]. Therefore, the tendency of wax crystals to interlock into a continuous network structure is impeded and the rheology of waxy crude oil is improved. Meanwhile, the VA content and the average molecular weight are the two key factors influencing the performance of EVA PPD [9,11]: the EVA containing VA content around 28 wt% usually has the best pour point depressing performance, while the optimal average molecular weight of EVA may be varied for different waxy crude oils.

Nowadays, polymer/inorganic nanocomposites have been prepared in large scale and widely used in industry due to their excellent mechanical stability, thermal stability and toughness, etc [13,14]. Inspired by the advances of polymer/inorganic nanocomposites, some kinds of polymer/inorganic nanocomposite PPDs were recently developed and evaluated. He et al. [15] prepared a nanocomposite PPD by dispersing nanoclays into an EVA PPD. They found that the nanocomposite PPD could further decrease the pour point and viscosity of a waxy crude oil based on the neat EVA PPD's performance. Yang and Norrman et al. [16,17] prepared a nanocomposite PPD by dispersing hydrophilic nanosilica into polyoctadecylacrylate (POA) PPD. They found that: (a) the prepared nanocomposite PPD can exist in oil phase as micro-sized composite particles (dozens of micron); (b) the composite particles can act as nucleation templates for wax precipitation and change the morphology of precipitated wax crystals into large spherical-like flocs, thus further improving the rheology of waxy oil; (c) the compatibility between the hydrophilic nanosilica and the organic POA PPD is poor and then the composite particles dispersed in oil phase are unstable, causing that the performance of the nanocomposite PPD decreases with time. In order to improve the compatibility between the inorganic nanoparticles and the polymeric PPDs, Yang et al. [18,19] first prepared organically modified nanoclays (abbreviated as organic nanoclays) through cationic exchange and then dispersed the organic nanoclays into POA PPD matrix. The obtained POA/organic clay nanocomposite PPD disperses well in oil phase as small composite particles (several microns) and the composite particles can also act as nucleation templates for wax precipitation. Therefore, the precipitated wax crystals' morphology is greatly modified after the addition of the nanocomposite PPD, resulting in the further improvement of waxy crude oil rheology. In addition, the time-effectiveness of the POA/organic clay nanocomposite PPD was also greatly improved. Al-Sabagh et al. [20,21] successfully prepared the poly(methylmethacrylate)/graphene oxide (PMMA/GO) and PMMA/montmorillonite (PMMA/MMT) nanocomposite PPDs by dispersing the inorganic nanosheets of GO or MMT in the organic PMMA matrix via in situ free radical polymerization. They found that the two nanocomposite PPDs disperse well in oil phase as small composite particles (several microns) and the performance of the two nanocomposite PPDs is much better than the neat PMMA PPD. They attributed the excellent performance of the two nanocomposite PPDs to the nucleation effect of the composite particles and the electrostatic repulsion between the composite particles.

Based on the research work mentioned above, it is clear that the polymer/inorganic nanocomposite PPDs have become a research hotspot in petroleum industry. In order to further develop the theory of nanocomposite PPDs, it is necessary to understand if the nano and micro particles alone can improve the rheology of waxy crude oil. Polysilsesquioxane (PSQ) microsphere is a kind of organosilicone materials, which has excellent morphological and structural properties [22–24]: the PSQ microsphere is normally monodispersed sphere with the size ranging from nano to micrometer; the PSQ microsphere has specific organic-inorganic hybrid structure, which imparts the PSQ microsphere outstanding thermal stability, mechanical stability, solvent resistance, lubricity, and excellent dispersiblity in organic solvents or polymers. Recently, Yang et al. [25] synthesized the polymethylsilsesquioxane (PMSQ) microsphere with different sizes and found that: (a) the PMSQ microsphere disperses well in oil phase as single spheres; (b) adding 50–400 ppm PMSQ microsphere can greatly improve the flow behavior of waxy crude oil; (c) the best dosage and size of the PMSQ microsphere are 200 ppm and 2–5 μm, respectively; (d) the PMSQ microsphere cannot participate in wax precipitation process and change the morphology of precipitated wax crystals, but can impede the interactions of the precipitated wax crystals through the spacial hindrance effect, which inhibits the development of wax crystal network structure and then improves the flow behavior of waxy crude oil; (e) however, the flow improving efficiency of the PMSQ microsphere is not as good as the traditional polymeric PPDs. Could it be possible to obtain a better flow improving efficiency by adding both the polymeric PPDs and the PMSQ microsphere into waxy crude oil? And if so, what is the synergistic mechanism?

To answer the questions mentioned above, in this paper, the effect of an EVA PPD together with a monodispersed PMSQ microsphere (with the size around 2 μm) on the flow behavior of a typical waxy crude oil is investigated. It is found that the neat PMSQ microsphere cannot improve the flow behavior of the oil at small dosages (≤10 ppm), but can significantly improve the performance of the EVA PPD (fixed at 50 ppm dosage). The performance improving mechanism of the PMSQ microsphere on the EVA PPD is also discussed based on the microscopic images of precipitated wax crystals and the adsorption behavior of EVA molecules onto the PMSQ microsphere.

2. Experimental

2.1. Materials

All the chemicals (including the EVA PPD) used here were purchased from Sigma-Aldrich Co., Ltd and used as received. The PPD used here is EVA2806, which has the best performance on the crude oil used in this work (performances of some other PPDs can be seen in the Table S1 of the support information). The VA content and the melting index of the EVA2806 are 28 wt% and 6, respectively. The PMSQ microsphere used here was synthesized based on the method mentioned in a previous paper [25]. As seen in Fig. 1, the synthesized PMSQ microsphere is monodispersed and