Fuel 220 (2018) 167–176

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 dosage of the amino-functionalized polymethylsilsesquioxane (PAMSQ) microsphere

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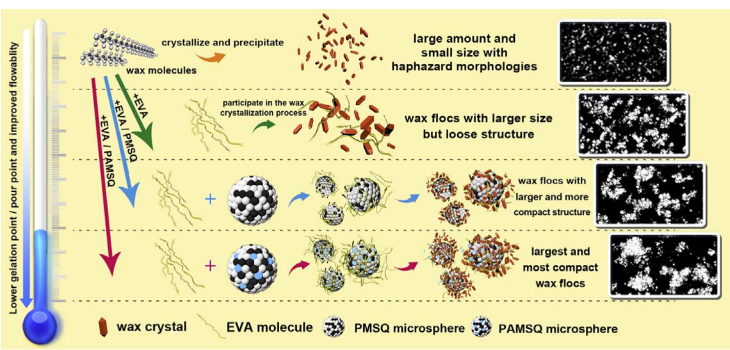
GRAPHICAL ABSTRACT



ARTICLE INFO

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

ABSTRACT

In the previous work, we have reported that small dosages of the polymethylsilsesquioxane (PMSQ) microsphere can effectively improve the performance of the EVA pour point depressant (PPD) and the amount of EVA PPD adsorbed on the microsphere evidently influences the efficiency of the EVA/PMSQ composite particle. To further promote the adsorption of EVA on the microsphere and enhance the efficiency of the composite particle, here, the amino-functionalized PMSQ microspheres with different amino molar ratios (PAMSQ) are first synthesized and characterized. The flow behavior, exothermic crystallization and microstructure of the waxy crude oil undoped/doped with EVA, EVA/PMSQ and EVA/PAMSQ are systemically investigated. Results show that 50 ppm EVA PPD can greatly improve the flow behavior of the oil and small dosages (2.5 ppm) of PMSQ microsphere can significantly improve the performance of the EVA PPD. After the amino-functionalization, the flow improving efficiency of EVA/PAMSQ is further enhanced: the gelation point, G', G'', apparent viscosity and yield stress of the oil sample decrease to a lower value. The best performance is found at adding 50 ppm EVA + 2.5 ppm PAMSQ-2 (with amino molar ratios at 15%). Compared to EVA/PMSQ, the EVA/PAMSQ exhibits a stronger nucleation effect to increase the WAT of the oil sample slightly, and outstandingly modifies the morphology of the precipitated wax crystals into larger and more compact flocs. The amino-functionalization facilitates more EVA PPDs adsorbing and concentrating on the PAMSQ microsphere, causing the formation of the EVA/PAMSQ composite particles. The composite particles provide stronger nucleation effect for the wax precipitation, resulting in larger and more compact wax microstructures and then further improving the flow behavior of the oil. The rheological improving performance of EVA/PAMSQ for the waxy crude oil increases with the increase of

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https://doi.org/10.1016/j.fuel.2018.01.032
Received 8 September 2017; Received in revised form 20 November 2017; Accepted 9 January 2018

amino molar ratio and the efficiency of EVA/PAMSQ-2 reaches the best. When the amino molar ratio is too high (PMASQ-3), the PAMSQ-3 microsphere is unstable in oil phase and aggregates into large particle flocs, which inhibits the EVA adsorption on the PAMSQ-3 microsphere and then weakens the rheological improving efficiency of the EVA/PAMSQ-3 composite particle.

1. Introduction

The waxy crude oil, which contains a substantial amount of paraffin waxes with the carbon number range from C_{18} to C_{40}, is an important fossil fuel resource widely spread all over the world. When the waxy crude oil is cooled below its wax appearance temperature (WAT), the wax molecules start to precipitate and crystallize from the oil [1]. Due to the large aspect ratio (plate-like or needle-like) [2–4], the precipitated wax crystals are liable to interlock with each other and form a continuous network structure, thus greatly aggravating the waxy crude oil rheology (impairing the flowability, or worse, causing the gelation of the oil). The aggravated flowability decreases the efficiency of the pipelines transporting waxy crude oil, while the security of the pipelines during a restart process would deteriorate due to the gelation of the oil.

To improve the efficiency and security of the pipelines transporting waxy crude oil, the most commonly used method is to pretreat the waxy crude oil with polymeric pour point depressants (PPDs) [1,2,5]. The molecular structure of polymeric PPDs normally contains both the non-polar moieties and the polar moieties [6–8]. The non-polar moieties, which are usually long alkyl chains, can take part in the precipitation process of paraffin waxes, while the polar moieties such as ester group, maleic anhydride group and vinyl acetate (VA) group, can interfere the growth of wax crystals [7,9–11]. To date, the polymeric PPDs could be classified into two types [1]: the linear copolymers and the comb-like copolymers. For the linear copolymers, such as poly(ethylene-co-vinyl acetate) (EVA), the long alkyl chains are located in the backbone; for the comb-like copolymers such as polymethylacrylate, poly(styrene-co-octadecyl maleimide) and acrylate copolymers, the long alkyl chains are mainly located in the side chain [6,9,10–14]. EVA is a kind of effective polymeric PPDs and has been widely studied as model PPD due to its explicit molecular structure. The efficiency of EVA PPD is greatly affected by the factors like the content of VA, molecular weight of EVA, composition and content of wax, etc. The pour point depressing mechanism of the EVA PPD was also discussed based on the microscopic observation, DSC analysis, XRD, and molecular dynamic simulation [12,13,15–17]. In general, the EVA PPD can control the morphology of waxy crystals and the interaction between them, thus improving the rheology of waxy crude oil.

Enlightened by the excellent performance of the polymer/inorganic nanocomposites, recently, different kinds of inorganic nanoparticles have been introduced into the traditional polymeric PPDs' matrix to prepare the nanocomposite PPDs [18–24]. Several techniques have been employed to prepare the nanocomposite PPDs, including solvent blending, melt blending, and in situ free radical polymerization [18–24]. By dispersing the silica, clay and graphene oxide into the matrix of polymeric PPDs, different kinds of nanocomposite PPDs were successfully prepared and the performance of them were also investigated through rheological test, DSC analysis and microscopic observation [18–24]. The results showed that (a) the prepared nanocomposite PPDs disperse in oil phase as micro-sized aggregated particles, and the composite particles can act as nucleation templates of wax crystals, thus further modifying the precipitated wax crystals' morphology and improving the rheology of waxy crude oil; (b) organic modification of the inorganic nanoparticles improves the compatibility between the inorganic nanoparticles and the polymeric PPDs, thus facilitating the dispersion of the nanoparticles in polymeric PPDs' matrix and favoring the performance improvement of the nanocomposite PPDs; (c) compared to solvent blending technique, melt blending technique is easier to disperse nanoparticles into the polymeric PPDs' matrix, therefore, the nanocomposite PPDs prepared by melt blending are superior to those prepared by solvent blending. However, the composite PPDs prepared by the three techniques mentioned above are energy consuming and need precise control during the preparing process. In addition, the prepared composite PPDs need to be re-dispersed into oil phase before usage, which also complicates the application of the composite PPDs in real crude oil pipelines. Is it possible to prepare the composite PPDs directly in oil phase through a convenient way?

Polysilsesquioxane (PSQ) microsphere is a kind of organosilicone materials with the molecular structure of $RSiO_{3/2}$, where R represents the organic groups such as methyl, phenyl, mercapto, amine, epoxy acrylic and isocyanate. With the specific organic-inorganic hybrid structure and regular morphology (mono-dispersed sphere with size ranging from nano- to micro-meter), PSQ microsphere has been widely applied in chemistry and physic fields [25–29]. Recently, Yang et al. [30,31] synthesized the polymethylsilsesquioxane (PMSQ) microsphere with different sizes (200 nm ~ 10 μm) and evaluated its efficiency as a flow improver for waxy crude oil. It was found that the PMSQ microsphere disperses well in oil phase as single sphere and adding the PMSQ microsphere (50–400 ppm) alone can improve the flowability of waxy crude oil through the spacial hindrance effect. However, the flow improving ability of the PMSQ microsphere is far below the traditional polymeric PPDs, and the PMSQ microsphere takes effect only under static cooling/isothermal conditions [31]. In another work, Yang et al. [32] first dissolved/dispersed 5 wt% EVA PPD and a small amount of the PMSQ microsphere (around 2 μm, 0.05 ~ 1 wt%) in *n*-dodecane. Then, they added the solution/dispersion containing both EVA PPD and PMSQ microsphere into a waxy crude oil. The dosage of EVA was fixed at 50 ppm, while the dosage of PMSQ microsphere is ≤ 10 ppm. It was found that (a) adding ≤ 10 ppm PMSQ microsphere alone in the waxy crude oil cannot improve the flow behavior of the oil; (b) the EVA molecules can adsorb and concentrate on the PMSQ microsphere, thus directly forming composite particle PPD in *n*-dodecane; (c) the composite particle PPD can act as the nucleation template for wax precipitation, thus greatly modifying the precipitated wax crystals' morphology and further improving the performance of the EVA PPD; (d) the best dosage of the PMSQ microsphere is found to be around 2.5 ppm; (e) the amount of EVA adsorbed on the PMSQ microsphere greatly affects the performance of the composite particle PPD. Obviously, this work provide a convenient method to directly prepare the composite PPDs in oil phase, which has practical application in the real pipelines transporting waxy crude oil.

In this paper, the amino-functionalized polymethylsilsesquioxane (PAMSQ) microspheres with different amino molar ratios (0 ~ 25 mol %) were first synthesized and characterized. Then, the effect of the EVA PPD together with the PAMSQ microsphere (with the size around 2 μm) on the flow behavior of a typical waxy crude oil was investigated. The results showed that compared to the PMSQ microsphere, the PAMSQ microsphere could further improve the performance of EVA PPD and the amino molar ratio of the PAMSQ dominants its performance. Associated with the exothermic property, the microstructure of the undoped/doped waxy crude oils and the adsorption behavior of EVA PPD on PAMSQ microsphere, the performance improving mechanism of the PAMSQ microsphere on the EVA PPD was also discussed here.