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Organically modified nano-clay facilitates pour point depressing activity of polyoctadecylacrylate

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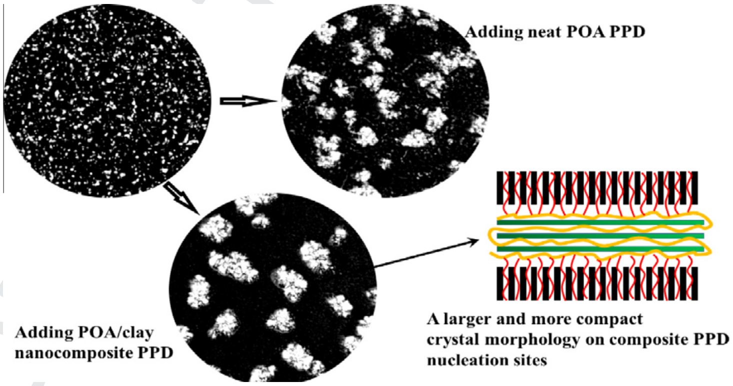
HIGHLIGHTS

- We introduce organic nanoclay to prepare nanocomposite pour point depressant.
- POA/clay nanocomposite could further improve the rheological properties of crude oil.
- The addition of nanoclay fosters the precipitation of wax crystals.
- Adding nanocomposite PPD results in the formation of larger and compact wax crystals.
- A possible heterogeneous nucleation mechanism for POA/clay nanocomposite is proposed.

GRAPHICAL ABSTRACT

Introduction of nanomaterials constitutes a novel and efficient means to enhance the performance of polymeric pour point depressants (PPDs). Based on the specific layered structure and favorable cationic exchange characteristics of nano-clay particles in the presence of charged organic compounds, an original hydrophilic nano-clay is first modified by octadecyltrimethyl ammonium chloride (OTAC) and then bypolyoctadecylacrylate (POA). The modified nano-clay serves as an effective nanocomposite PPD. Compared to an identical content of POA, addition of POA/clay nanocomposite PPD to Changqing waxy crude oil improves the rheological properties while elevating the wax appearance temperature of the oil. Polarized microscope observation shows that POA/clay nanocomposites provide wax nucleation sites upon which wax molecules assemble and precipitate. Addition of POA/clay nanocomposite PPD results in larger and more compact crystal morphology, thus inhibiting the formation of a network structure, and further improving rheological properties of waxy crude oil.



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ABSTRACT

Introduction of nanomaterials constitutes a novel and efficient means to enhance the performance of polymeric pour point depressants (PPDs). Based on the specific layered structure and favorable cationic exchange characteristics of nano-clay particles in the presence of charged organic compounds, an original hydrophilic nano-clay is first modified by octadecyl trimethyl ammonium chloride (OTAC) and then by polyoctadecylacrylate (POA). The modified nano-clay serves as an effective nanocomposite PPD. Compared to an identical content of POA, addition of POA/clay nanocomposite PPD to Changqing waxy crude oil improves the rheological properties while elevating the wax appearance temperature of the oil. Polarized microscope observation shows that POA/clay nanocomposites provide wax nucleation sites

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Waxy crude oil
POA
Nano-clay
Nanocomposite

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1. Introduction

Precipitation of paraffin waxes with carbon numbers C_{16}–C_{40} from waxy crude oils greatly complicates the low temperature flow properties of the oils, generating difficulties in pipeline transportation of the oils [1,2]. A well-recognized and efficient solution to these problems is deployment of polymeric additives such as pour point depressants (PPDs) and flow improvers (FIs) [3]. PPDs/FIs doped in waxy crude oils could modify crystal growth habits by nucleation, adsorption and co-crystallization effects, effectively inhibiting the tendency of wax crystals to interconnect into fixed three-dimensional networks [4,5]. Consequently, pour point, viscosity and yield stress values of waxy crude doped with PPDs/FIs are substantially reduced.

1 Comb-like polymers, such as polyacrylates and alkyl maleic anhydride copolymers, have been thoroughly studied as PPDs of waxy crude oils and diesel oils. Effects of alkyl side chain length, polar group type and content, molecular weight, oil phase composition on the efficiency of comb-like PPDs have been elucidated [6–9]. Results show that alkyl chain length is a crucial factor influencing the efficiency of comb-like PPDs. In addition, some researchers added polar groups and benzene rings to structure of comb-like PPDs to enhance interactions with asphaltene, which is shown to increase the field performance of the PPDs [10]. Poly (octadecyl acrylate) (POA) is an effective comb-like PPD for waxy crudes, appearing to favor formation of island defects on paraffin wax surfaces, which exhibit weak interactions with the surrounding crystal and, therefore, act as impurity sites for blocking growth steps [11,12]. Although the poly (octadecyl acrylate) has been widely applied in pipe transport of waxy crude, its efficiency needs further improvement [5].

With the recent development of nanotechnology, polymer/inorganic nanocomposites or nano-hybrid materials have become the focus of significant R&D endeavors in the 21st century [13,14]. By introducing inorganic nanoparticles into polymeric matrices, resultant properties (i.e. mechanical, thermal, magnetic, and electrical) are vastly improved. Enlightened by advances in polymer/inorganic nanocomposites, researchers developed nano-hybrid PPDs by dispersing nanoparticles into polymeric PPD matrices. Wang et al. [15] prepared a nano-hybrid PPD and compared its efficiency with traditional ethylene vinyl acetate (EVA) PPDs. Rheological results showed that nano-hybrid PPD exhibits improved pour point depression efficiency in comparison to the corresponding EVA. Yang et al. [16] prepared a nano-hybrid PPD by directly dispersing hydrophilic nano-silica into POA PPDs. Compared with POA-based PPDs, nano-hybrid PPD further reduces gelation point, viscosity and yield stress of synthetic waxy oils. Microscopic images of precipitated wax crystals demonstrate that POA/nano-silica hybrids provide spherical-like templates for wax precipitation, imparting a large and compact morphology of precipitated wax crystals, suppressing gelation and improving flowability of the oil. The authors also observed in the experiment that the efficiency of nano-hybrid PPD was not stable and decreased with rest time to the efficiency of pure POA in the end. This was perhaps because POA molecules adsorbed on the surface of silica desorb into oil phase due to the incompatibility of hydrophobic POA molecules and hydrophilic nano-silica. Therefore, the surface of nano-particles should be properly modified so as to strengthen interaction between polymeric PPDs and nano-particles.

Montmorillonite (MMT) nano-clay is a layered silicate mineral with a 2:1 type layer structure, i.e., it has two tetrahedral sheets sandwiching a central octahedral sheet [17]. Due to isomorphous substitution, the nano-clay is negatively charged and some hydrated Na^+ or K^+ species exist in the interlayer in order to balance the negative charge [18]. Surfactants such as quaternary ammonium salt surfactants, are often used to modify nano-clay such that organic cations replace the interlayer hydrated Na^+ or K^+, i.e., cation exchange, enlarging layer spacing and enhancing lipophilicity of the nano-clay. In this way, the organic nano-clay (abbreviated as organic nano-clay) is easier to disperse in a polymer matrix. In past decades, organic nano-clay has been introduced into polymer matrices to form polymer/clay nanocomposites (PCN) [19,20]. Due to imbibed nano-clay, PCN properties such as mechanical strength and thermal tolerance are superior to those of pristine polymers. Because of the specific layered structure and simple organic modification of MMT nano-clay, a POA/MMT clay nanocomposite PPD is developed in this work. Rheological beneficiation for Changqing waxy crude oil is evaluated. The nano-clay is first organically modified by cation exchange to improve its lipophilicity and to enhance the interaction between nano-clay and POA. Subsequently, POA/clay nanocomposite is prepared by solvent blending. The effect of POA/clay nanocomposite PPD on wax appearance temperature (WAT), rheological parameters, and morphology of precipitated wax crystals of Changqing waxy crude oil is thoroughly investigated by DSC, rheometry and microscopic observation. The beneficiation mechanism of nanocomposite PPD on crude oil rheology is also discussed.

2. Experimental section

2.1. Materials

Deionized water was purified by reverse osmosis. Dodecane, toluene, ethanol, octadecyl acrylate, octadecyl trimethyl ammonium chloride (OTAC) and 2,2′-Azobis(2-methylpropionitrile) (AIBN) were purchased from Sinopharm Chemical Reagent Co. of China. Chemical purities were all analytical or chemical pure grade (with the purity $\geqslant 98$ wt%). The comb-like POA PPDs were synthesized by solvent free-radical polymerization of octadecyl acrylate under a nitrogen atmosphere with AIBN as the initiator and toluene as the solvent [16]. The average molecular weight of POA tested by gel permeation chromatography (GPC) was ~20,000 Da. MMT nano-clay was purchased from Hengshi Mineral Processing Co. in China. The cation exchange capacity (CEC) of nano-clay is ~98 mmol/100 g.

The crude oil was kindly provided by Changqing oilfield in China. As shown in Table 1, the crude oil contains a large content of saturates (66.89 wt%) and aromatics (23.51 wt%), while the content of resins (8.78 wt%) and asphaltenes (0.82 wt%) are relatively small. The initial boiling point of the crude oil is relatively low (56 °C), while the wax content (15.35 wt%) and pour point (28 °C) is relatively high. Fig. 1 shows the crude oil has a wide *n*-alkane distribution (C_8–C_{45}) with the peak carbon number around C_{18}.

2.2. Preparation of organic nano-clay

Hydrophilic nano-clay was modified by OTAC via cationic exchange. According to previous research [21,22], the OTAC con-

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