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Influence of poly (methacrylate-co-maleic anhydride) pour point depressant with various pendants on low-temperature flowability of diesel fuel

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HIGHLIGHTS

- C_{14}MC-MA-14a had a better effect on reducing CFPP when using a single PPD.
- C_{14}MC-MA-phenylamine had a good effect on SP when using a single PPD.
- PPDC-1 exhibited the best depression on SP and CFPP at a concentration of 1000 ppm.
- The mechanism of the interaction between the PPDs and the $0^{\#}$ diesel was elucidated.

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ABSTRACT

To investigate the influence of various pendants in comb-type copolymers on the low-temperature flowability of diesel fuel, a series of methacrylate-co-maleic anhydride copolymers R_1MC-MA ($R_1 = C_{14}$, C_{16}, C_{18}) were synthesized. And C_{14}MC-MA was aminated by R_2NH_2 ($R_2 = C_{14}$, C_{16}, C_{18}, phenyl, 1-naphthyl) to obtain a series of aminated copolymers C_{14}MC-MA-a (C_{14}MC-MA-14a, C_{14}MC-MA-16a, C_{14}MC-MA-18a, C_{14}MC-MA-phenylamine, C_{14}MC-MA-naphthylamine). They were characterized by Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (1H NMR) and gel permeation chromatography (GPC). The influence of these pour point depressants (PPDs) on the cold flow properties of diesel fuel were investigated. The crystallization behavior and crystal morphology of diesel fuel were also studied by differential scanning calorimeter (DSC) and polarizing optical microscope (POM). When the dosage of PPDs was 1000 ppm, C_{14}MC-MA-14a displayed an excellent depression on cold filter plugging point (CFPP) by 5 °C, C_{14}MC-MA-phenylamine showed the best depression on solid point (SP) by 17 °C, and PPDC-1 (the mixture of C_{14}MC-MA-14a with C_{14}MC-MA-phenylamine) exhibited the best performance in depressing the CFPP and SP by 8 °C and 18 °C respectively. The results show that the effects of the PPDs on reducing SP and CFPP sometimes are inconsistent, because SP is closely related to the crystal/liquid interface, while CFPP is directly related to the wax crystal size. When pour point depressants are added, the wax crystals become smaller and regular (act as wax dispersants), thus inhibiting the formation of the porous network. So the CFPP decreased with decreasing the wax crystal size; and the SP first decreased with decreasing the wax crystal size, while when the wax crystals are too small, the large specific surface energy leads to the recovery of the SP. DSC and POM results showed that PPDs changed the crystallization behavior, size and shape of wax crystals, weakened the ability of wax crystals to form a three-dimensional network structure and made the wax crystals more uniform, compact, and dense. Therefore, the low temperature flowability of diesel fuel is improved by the synthesized pour point depressant.

1. Introduction

Diesel fuel, which contains a substantial amount of paraffin waxes, is the most widely used fuel in industrial diesel engines, ships and thermal power plants. The dissolved paraffin waxes start to crystallize into solid wax crystals from diesel oil when the

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temperature of waxy oil is lower than its wax appearance temperature. (WAT) The wax crystals are liable to grow into large and irregular particles (plate-like or needle-like). The big wax crystals are not easy to get through the filter, so the large precipitated wax crystals effect on the CFPP of diesel fuel. With the further decrease of oil temperature, the large plate-like or needle-like wax crystals are easier to cross-link into a house-of-card structure by the van der waals forces. The oil present around this network gets trapped in it, and below the cloud point, it results in a gel-like structure [1–3]. As a result, the diesel fuel has a high viscosity, which affects the normal use and transportation of diesel fuel [4–8].

To overcome such cold flow difficulties, a well-recognized and efficient way is the use of small dosages of polymeric additives which are often known as pour point depressants (PPDs) [8–12]. They are the high molecular weight organic polymers that can change the crystalline form of wax crystals and improve the rheological properties of diesel. Conventional PPDs are usually homo- and co-polymers of different monomers [13–16]. The nonpolar moieties of the PPDs are normally long alkyl chains which interact with paraffin waxes via nucleation, adsorption or co-crystallization effect. The co-crystallization effect plays a more important role; while the polar moieties may expose on the surface of precipitated wax crystals, interfering with the precipitation process of waxes and changing the morphologies of wax crystals [1,4,9].

Various types of polymeric additives have been developed and used as PPDs to reduce the pour point of diesel fuel. The most commonly used PPDs mainly including poly (ethylene-co-vinyl acetate) (EVA) [13,17–19], α-olefin copolymer [20–22], poly (ethylene-butene) (PEB) [23], poly (alkyl methacrylates) [16] and modified maleic anhydride (MA) polymers [24]. The PPDs can be categorized as Crystalline-amorphous polymers, EVA type and comb-like PPD, and more attention was paid to comb-like polymers [25–28]. The effect of polymer molecular weight, alkyl side chain length [17,28] and polar group type and content [11,27,28] of comb-like PPDs have been elucidated. Results show that alkyl chain length is a crucial factor influencing the efficiency of comb-like PPDs [5,6,29]. In addition, it is common to introduce a suitable content of polar groups [24,28] (such as maleic anhydride, aminate, vinyl acetate, etc.) and benzene rings into the backbone of the comb-like PPDs to improve the performance of the PPDs.

The effect of relating maleic anhydride PPDs on the cold flow properties of diesel fuel were reported in some works [4–6]. Song et al. [5] have reported the relationship between the structure and activities of alkyl methacrylate-maleic anhydride polymers as cold flow improvers in diesel fuel. Copolymers (R^1MC-MA) and terpolymers (R^1MC-MA-R^2MC) were prepared (R^1MC, $R^1 = C_{12}$, $C_{14,}$ C_{16} or C_{18}; R^2MC, $R^2 = C_1$, C_2, C_4 or C_8). Results showed that when the long-chain alkyl R^1 is n-$C_{14}H_{29}$- and the reaction material molar ratio (R^1MC/MA) is 1:2, the C_{14}MC-2MA possesses the best ΔSP property, whereas the copolymer with n-$C_{12}H_{25}$- or n-$C_{18}H_{37}$- almost has no solid point depression performance; C_{14}MC-MA-R^2MC terpolymers all demonstrate excellent solid point depression properties when the short-chain alkyl R^2 varies from CH_3- to n-C_8H_{17}-, and while all of the tested copolymers and terpolymers could not obviously improve the CFPP of diesel fuel. It is thus concluded that: (1) the n-$C_{14}H_{29}$- alkyl chain is the optimal matching alkyl chain for preparing the cold flow improvers suitable to the tested basic fuels; (2) a good cold flow improver only needs weak polarity rather than nonpolarity or high polarity, because when the polar groups are excess in the molecules, they hinder the co-crystallization of the polymer with the n-paraffins in the diesel fuel; (3) the polymer containing short-chain alkyl can promote the polymer to co-crystallize with the n- paraffins in the fuel. Han et al. [4] have studied the impact of alkyl methacrylate-maleic anhydride copolymers as pour point depressant on crystallization behavior of diesel fuel. Tetradecyl methacrylate-maleic anhydride-methyl methacrylate terpolymers (MC_{14}-2MA-MC_1, MC_1, C_1=C_1, C_2, C_4 or C_8) is selected as the representative cold flow improver in this experiment. Adding the C_{14}MC-2MA-MC_2 by 500 ppm, the SP and CFPP of diesel fuel decreased by 19 °C and 2 °C, respectively. The results showed that the crystallinities of the high carbon number n-alkanes show a decrease after adding C_{14}MC-2MA-MC_1. Feng et al. [6] have carried out the synthesis and evaluation of alkyl acrylate-vinyl acetate-maleic anhydride terpolymers (AVM) as cold flow improvers for diesel fuel, and the n-alkyl acrylates were R^1MC (R^1 = 12, 14, 16, 18). Among these terpolymers, AVM-16 is most successful in reducing CFPP (reduces the CFPP by 5 °C) and has a better effect on reducing SP; AVM-14 exhibits the most considerable reduction on SP, which can reduce the SP and CFPP by 16 °C and 2 °C, respectively at a concentration of 0.25 wt%. AVM-18 has a moderate effect on SP and CFPP, while AVM-12 almost has no effect on both. It is concluded that the influence of n-alkyl chain length of terpolymers is closely related to the content of the corresponding n-alkane in the diesel fuel, especially for their influence on the SP, the n-$C_{14}H_{29}$–alkyl chain is the optimal matching alkyl chain for preparing the cold flow improvers suitable to the tested diesel fuel. These results are meaningful for improving the flow properties of diesel fuel. However, an additive typically does not perform equally in distinct diesel fuels, so it is necessary to enable development of additives that are less expensive and tailored to particular diesel fuel.

In this work, we have synthesized a series of methacrylate-maleic anhydride copolymers and aminated derivatives and evaluated the influence of various pendants in comb-type copolymers on the cold flow properties of $0^{\#}$ diesel fuel. Moreover, differential scanning calorimeter (DSC) measurements and microscopic observation by polarizing optical microscope (POM) of the treated and untreated systems were performed to study the crystallization behavior and the change of size, shape and aggregation of wax crystals.

2. Experimental

2.1. Materials

The copolymers (R_1MC-MA and C_{14}MC-MA-a) were synthesized and purified in a laboratory. Moreover, other substances were purchased from Sinopharm Chemical Reagent Co., Ltd., China, and employed without further purification: 1-tetradecanol, 1-hexadecanol, 1-octadecanol, methacrylic acid, maleic anhydride (MA), *p*-toluenesulfonic acid (PTSA), 1-tetradecylamine, 1-hexadecylamine, 1-octadedecylamine, phenylamine, 1-naphthylamine, hydroquinone, toluene, benzoyl peroxide, and sodium carbonate anhydrous. The substances used were analytical grade reagents. $0^{\#}$ diesel fuel, which meeting the requirements of the GB252 specification in the Chinese market, was obtained from the Shanghai Songjiang gas station (one of the point-of-sale of Sinopec Group, Shanghai).

2.2. Synthesis of N-alkyl acrylates

The n-alkyl acrylates were synthesized by the reaction of methacrylic acid and different n-alkyl alcohols (n = 14, 16, 18) in a molar ratio 1.2:1, using toluene as solvent, hydroquinone as inhibitor, PTSA as catalyst, water was separated azeotropically using Dean-Stark apparatus. The end products alkyl methacrylate (R_1MC) obtained were either a light yellow or milky white latex substances [30–34]. The synthesis routine of n-alkyl acrylates was showed in Fig. 1.