



Synthesis and evaluation of alkyl acrylate-vinyl acetate-maleic anhydride terpolymers as cold flow improvers for diesel fuel



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ABSTRACT

Four different alkyl chain length of n-alkyl acrylate-vinyl acetate-maleic anhydride terpolymers were synthesized by radical polymerization and characterized by FTIR and GPC. To further the development of these cold flow improvers, their performance mechanism was studied. The carbon number distribution of n-alkanes in 0# diesel fuel was analyzed by GC. The rheological behavior and crystallization behavior of diesel fuel treated with and without additives were studied using an advanced rheometer and an optical microscope. The results show that the influence of alkyl chain length of terpolymer was closely related to the content of the corresponding n-alkane in the diesel fuel. Besides, the formation of three-dimensional network directly determines the solidifying point of diesel fuel, while the cold filter plugging point is closely related to the size, shape and aggregation of wax crystals, thus the effects of cold flow improver on the solidifying point and cold filter plugging point of diesel fuel are sometimes inconsistent. Moreover, a good diesel cold flow improver should be detrimental to the formation of three-dimensional network and detrimental to the formation of too large wax crystals or wax crystals tending to form large clusters.

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1. Introduction

Diesel is a fuel derived from petroleum and mainly contains mixtures of hydrocarbon chains in the range of C8 to C30 [1]. The hydrocarbon has an important influence on the transportation of diesel fuels and operability of diesel engines [2]. At low temperatures, the solubility of hydrocarbon is decreased, so the hydrocarbon tends to be separated from the oil and the attraction of the waxy hydrocarbon segments toward each other due to Van der Waals forces results in the formation of wax crystals [3,4]. The paraffin crystals grow as the temperature decreases, creating a crystalline net thereby entrapping the remaining fuel in cage-like structures and causing the cold flow problems [5,6].

Adding pour point depressants (PPDs) to improve the cold flow properties of oils has been proven to be an effective and economic way [7]. In general, these additives have a wax-like paraffin part which provides the interaction between the additive and paraffin and a polar segment that is responsible for modifying the morphology of wax crystals [8–11]. Some characteristics of the additives should be considered: there should be a sufficient number of pendant alkyl groups with sufficiently long hydrocarbon chains, there should be an appropriate distance between the hydrocarbon pendant chains and there should be a suitable ratio of monomers for copolymer additives [12,13].

Many experimental and theoretical studies have been performed to reveal the pour point depressant mechanism and many hypothetical mechanism theories have been formed, in which adsorption, co-crystallization, nucleation, and improved wax solubility are the most widely accepted viewpoints [14–19]. Co-crystallization theory is that the nonpolar part of PPD molecules co-crystallizes with wax molecules at wax appearance temperature, while the polar part hinders the wax crystals further growth; Adsorption theory is that wax molecules first crystallize, then PPD molecules adsorb on the surface of the wax crystal particles and change the surface properties by the effect of polar groups; Nucleation theory is opposite to adsorption theory, it considers that PPD molecules first crystallize and become the nuclei of wax growth; Improved wax solubility theory is that PPDs can improve the solubility of wax in the oil, so that they can reduce the amount of wax precipitation. These theories are different and they are still disputed by researchers [16,20]. To completely understand the mechanisms, further studies are necessary.

In the present study we have synthesized four alkyl acrylate-vinyl acetate-maleic anhydride terpolymers with different long-chain alkyls by free radical polymerization and evaluated their influence on the flow properties of ordinary 0# diesel fuel. We also determined the carbon number distribution of n-alkanes in the diesel fuel and studied the rheological behavior and crystallization behavior of diesel fuel with and without additives. One of the purposes of this research was to observe the relationship between the influence of n-alkyl chain length of terpolymer and the n-alkanes in diesel fuel. Another purpose

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was to study the influence of size, shape and aggregation of wax crystals on solidifying point (SP), cold filter plugging point (CFPP) and viscosity.

2. Experimental methods

2.1. Materials

The following substances were purchased from Sinopharm Chemical Reagent Co., Ltd., China, and employed without further purification: 1-dodecanol, 1-tetradecanol, hexadecanol, octadecanol, acrylic acid, vinyl acetate, maleic anhydride, hydroquinone, p-toluenesulfonic acid, benzoyl peroxide, toluene, anhydrous ethanol and sodium carbonate anhydrous. The substances used were analytical grade reagents except for benzoyl peroxide (chemical grade). The ordinary 0[#] diesel fuel was supplied by Qingdao Refinery Co.

2.2. Synthesis of n-alkyl acrylates

The n-alkyl acrylates were prepared by the reaction of acrylic acid and different n-alkyl alcohols ($n = 12, 14, 16, 18$) in a molar ratio 1.2:1, using toluene as solvent, p-toluenesulfonic acid (PTSA) as catalyst, hydroquinone as inhibitor, water was separated azeotropically using Dean–Stark apparatus [13]. The alcohol, toluene and hydroquinone were added to a four-necked flask, then heated to 60 °C. After the alcohol completely dissolved, acrylic acid and PTSA were added, and gradually heated to 115–120 °C. The reaction was stopped after a theoretical amount of water separation. Reaction products were washed several times with an aqueous solution of Na₂CO₃ (5 % m/V) until the underlayer liquid became clear, then washed by distilled water, at last vacuum distilled using a rotary evaporator and vacuum dried.

2.3. Synthesis of terpolymers

The above synthesized n-alkyl acrylate, vinyl acetate and maleic anhydride dissolved in toluene in a 1:1:1 mol ratio were taken in a four-necked flask [8]. At the beginning, the contents were subjected to nitrogen flushing for twenty minutes, then gradually heated to 95 °C. When the temperature of the reaction reached 95 °C, benzoyl peroxide dissolved in toluene as an initiator was added drop by drop. The whole content was refluxed for 8 h. Finally, the thick slurry was distilled under reduced pressure, followed by precipitation in excess ethanol and vacuum dried for 24 h [21]. The reaction steps are as shown in Scheme 1. The prepared additives are named as AVM-12, AVM-14, AVM-16 and AVM-18, respectively.

2.4. Solidifying point and cold filter plugging point measurements

The synthesized pour point depressants always were first dissolved in toluene or xylene, then tested as PPDs. F. Vazquez et al. [22] prepared their polymer solution at 20 wt% of terpolymer in toluene and M.Z. Elsabee et al. [23] prepared their polymer solution at 10 wt% of copolymer in xylene. Due to the dosage of PPDs is very low in test, the dosage

of solvent is also very low. Thus the solvent used to dissolve PPDs almost has no effect on the results. Therefore our polymer solutions were prepared at 30 wt% of terpolymer in toluene. Terpolymers were added into the diesel fuel in different dosages (0.05 wt%, 0.10 wt%, 0.15 wt%, 0.20 wt% and 0.25 wt%, the mass ratio of pure terpolymer and diesel fuel). The mixture was placed in a 50 °C water bath for half an hour and at the same time was stirred to guarantee complete dissolution of the additives. Then solidifying point and cold filter plugging point were determined according to GB/T510-83 and SH/T0248-92 standard methods.

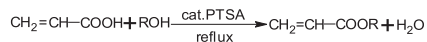
The brief steps of measuring SP were that: The sample was first heated to 50 ± 1 °C, then at room temperature cooled down to 35 ± 5 °C (for each test, the sample must be re-heated and cooled). Then the sample was placed in the cooling bath of the test instrument. When the sample temperature reached the expected solidifying point, the cooling bath was tilted 45 degrees and held for 1 min, then observed whether the liquid level of the sample had mobile signs. If the liquid level moved, the next test temperature was lower 4 °C than the previous. Conversely, the next test temperature was higher 4 °C than the previous, until the scope of the SP was identified. Then the selected test temperature was lower 2 °C than the temperature at which the liquid level moved, or was higher 2 °C than the temperature at which the liquid level did not move. The temperature at which the liquid did not move, an increase of 2 °C the liquid moved, was the SP of the sample.

The method of test CFPP was as follows: Cooling the sample under specified conditions, and making the sample get through a 363 mesh filter in 1961 Pa pressure. When the sample was cooled to a certain temperature, test was started whether the time of 20 mL sample to get through the filter was more than 60 s. If the time was less than 60 s, the sample was cooled at intervals of 1 °C, until the sample could not get through the filter or the time of 20 mL sample to get through the filter was more than 60 s. The highest temperature at which the sample could not get through the filter or the time of 20 mL sample to get through the filter was more than 60 s was the CFPP of the sample.

2.5. Gas chromatograph

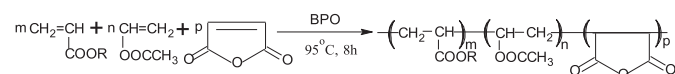
The distribution of n-alkanes with different carbon numbers in diesel fuel was analyzed using GC VARIAN CP-3800 apparatus. The mixed solution of nC14, nC15, nC16 and nC17 was used as the standard sample. The GC operating conditions were as follows: the temperature of the capillary column was procedurally raised by 6 °C/min from 100 °C to 300 °C, injector temperature (320 °C), detector temperature (340 °C) and the injection volume was 1 μL. The concentration distribution of n-alkanes in the diesel fuel is given in Fig. 1.

STEP-1



where R=12, 14, 16, 18

STEP-2



Scheme 1. Synthetic routine for the preparation of terpolymers.

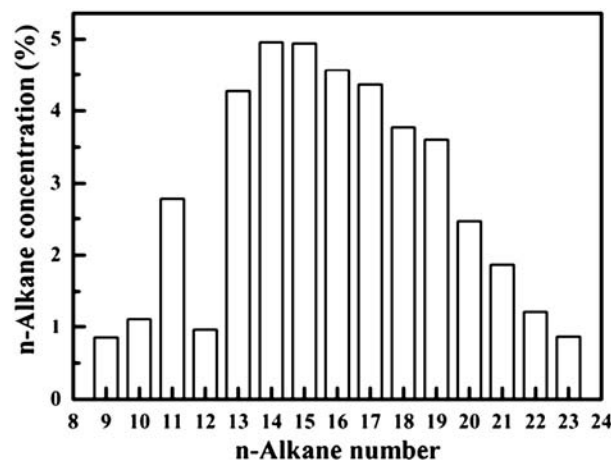


Fig. 1. Concentration distribution of n-alkanes in the diesel fuel.

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