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A new kind of nanohybrid poly(tetradecyl methyl-acrylate)-graphene oxide as pour point depressant to evaluate the cold flow properties and exhaust gas emissions of diesel fuels

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ABSTRACT

In this paper, a new kind of nanohybrid poly(tetradecyl methyl-acrylate)-graphene oxide (PMA_{14}-GO) as pour point depressant (PPD) was prepared from graphene oxide, using matrix via in situ free radical polymerization. The effect of PMA_{14}-GO (i.e., PMA_{14}-3GO, PMA_{14}-6GO and PMA_{14}-9GO) PPDs on the cold flow properties and exhaust gas emissions of diesel fuels were studied. Results indicated that PMA_{14}-GO PPDs exhibited a better effect on cold filter plugging point (CFPP) and solidifying point (SP) than that of PMA_{14}. Among them, PMA_{14}-6GO and PMA_{14}-9GO were the most suitable candidates for improving CFPP and SP. Specifically, upon addition of 0.2 wt% PMA_{14}-6GO could reduce the CFPP of diesel by 14 °C, and 0.2 wt% PMA_{14}-9GO reduced the SP of diesel by 19 °C. Moreover, PMA_{14}-GO PPDs could effectively lower the low-temperature. Other fuel properties were also determined and compared with the ASTM D975. Given the heterogeneous nucleation mechanism, uniform and tiny particle-shaped crystals were observed by polarizing optical microscopy and differential scanning calorimetry. In addition, burning diesel fuel with PMA_{14}-GO PPDs effectively reduced HC and CO emissions, whereas NO and CO_2 emissions increased with the increased engine speed at full load.

1. Introduction

In China, the diesel fuel requirement of people is further increasing because the combustion efficiency of diesel fuel is high. Therefore, the diesel fuel production must be increased [1]. However, the refining process in the distillation range of diesel fuel must be broad, thereby constantly increasing the number of carbon atoms that are composed of diesel fuel. Moreover, the molecular weight increases. Consequently, the low-temperature performance of diesel fuel is poor, and diesel fuel cannot satisfy the actual needs [2,3].

Currently, the pour point depressant (PPD) of diesel fuel is a commonly used method. The addition of simple and low-cost organic or inorganic hybrid polymer PPD has attracted considerable attention [4–6]. Yao et al. [4] prepared a polyoctadecylacrylate (POA)/clay nanocomposite PPD. They found that adding POA/clay nanocomposite PPD to Changqing crude oil could effectively improve the rheological properties. Norrman et al. [7] prepared the nanohybrid PPD by coating the silica nanoparticles coated with poly(octadecyl acrylate) (POA) and focused on the effect of a model waxy oil system. They found that the nanohybrid PPD could significantly lower the rheological properties of the wax gel strength when the silica nanoparticles are fully covered with POA. In addition, we also developed a nanohybrid PPDs with organically modified nanoclay covering in the polymeric PPDs [6]. Addition of nanohybrid PPDs to diesel fuel improves the cold flow properties of diesel fuel. Nanohybrid poly(methyl acrylate) (PMA) could reduce the cold filter plugging point (CFPP) and solidifying point (SP) by 16 and 14 °C, respectively. Although the nanohybrid PPD improves the rheological properties of crude oil and the cold flow properties of diesel fuel, it also presents remarkable disadvantage. According to our previous study, the nanomaterials of nanohybrid PPDs are commonly selected nanoclay, silica, and titania, which possess a poor oil solubility and dispersion [6–8]. Considering these properties, the nanohybrid PPDs cannot effectively improve the low-temperature performance of diesel fuel and achieve the desired results. Therefore, a nanomaterial with good oil solubility and dispersion should be determined to prepare a new kind of nanohybrid PPD.

Graphite oxide (GO), which is prepared by graphite, has a layered structure composed of parallel pseudo 2D lamellae, good oil solubility, and strong dispersibility [9–13]. In addition, GO is relatively similar to montmorillonite because of its intercalated or exfoliated structures in the polymer matrix to create a nanocomposite; thus, this material shows a broad application prospect in the field of nanocomposite

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materials [12–15]. Jang et al. [13] prepared graphite oxide GO/poly (methyl methacrylate) (PMMA) nanocomposites by a novel method utilizing macroazoinitiator; their results showed that the morphological, conductivity, thermal, mechanical, and rheological properties of GO-PMMA markedly improved compared with those of intercalated nanocomposites prepared by polymerization with the normal radical initiator, that is, 2,2-azobisisobutyronitrile. Alsabagh et al. [12] prepared a nanohybrids of PMMA-GO as PPD. After adding PMMA-GO nanohybrid to waxy crude oil, the pour point and the apparent viscosity were significantly reduced. Nevertheless, the effect of polymer/GO nanohybrid PPDs as a cold flow improver in diesel fuel has not yet been studied. Hence, it will be beneficial for the development of diesel PPD and polymer/GO nanocomposite and will effectively resolve the poor oil solubility and dispersion of traditional nanohybrid PPDs.

In the present study, GO is first introduced to combine with tetradecyl methyl-acrylate by matrix through in situ free radical polymerization as a nanohybrid PPD to improve the cold properties of diesel fuel. The effects of the PMA_{14}-GO nanohybrid PPDs on the CFPP and SP of diesel fuel were evaluated. Other important fuel properties, such as acid value (AV), kinematic viscosity (υ), oxidation stability (OS), and flash point (FP), were also examined and compared with those of ASTM D975 standard. Furthermore, the crystallization behavior and crystal morphology of diesel fuel were observed by viscosity–temperature curves, polarized optical microscopy (POM), and differential scanning calorimetry (DSC). The emission performances of PMA_{14} and PMA_{14}-GO nanohybrid PPDs on diesel fuel were also discussed.

2. Experimental

2.1. Materials

0# diesel fuel was purchased from the China Petrochemical Corporation. Graphite flakes (400 mesh) were purchased from Sigma Aldrich (USA). All chemicals including tetradecyl methyl-acrylate (MA_{14}, 99%), benzoyl peroxide (BOP, 75%), N, N-Dimethylformamide (DMF, 99.8%), $NaNO_3$ (99%), $KMnO_4$ (≥99.5%), H_2SO_4 (98%) and H_2O_2 (31%) were obtained from Aladdin Reagent Co., Ltd. (Shanghai).

2.2. Preparation of PMA_{14}-GO nanohybrid PPD

2.2.1. Preparation of GO

As shown in Fig. 1, GO was prepared from graphite flakes by following a modified Hummers method [16]. Graphite flakes (5 g) and $NaNO_3$ (3.75 g) were added into a 1000-ml flask, which contained concentrated distilled water (200 ml) with magnetic stirring for 1 h. Afterward, concentrated H_2SO_4 (150 ml) was slowly added to the flask with strong agitation for 1 h. $KMnO_4$ (20 g) was subsequently added into the mixture slowly with stirring for 35 min. The reaction lasted for five days until the solution was yellowish brown. Finally, the reaction was slowly added to the distilled water (500 ml) and H_2O_2 (30 ml) until the color gradually changed from yellow to bright yellow, and many bubbles were produced. The solution was centrifuged at 10,000–3000 rpm for eight times. The foam GO was obtained by vacuum drying for 72 h.

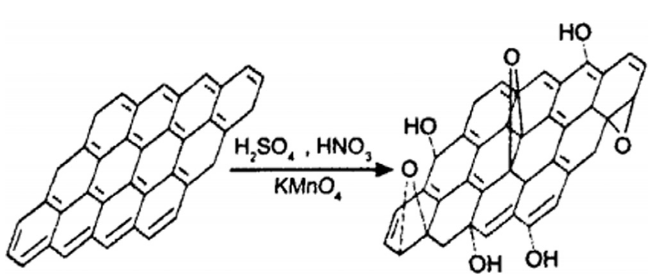

Fig. 1. Process of oxidation to graphene oxide with graphite flakes.

2.2.2. Preparation of PMA_{14}-GO nanohybrid PPDs

The PMA_{14}-GO nanohybrid PPDs were prepared by matrix via in situ free radical polymerization [13,15]. GO (3 mg) was ultrasonically dispersed in DMF (6 ml) for 5 h at room temperature. In a 250-ml flask, the GO/DMF suspension was purged with dry nitrogen for 30 min. The MA_{14} monomer (0.2 mol) and benzoyl peroxide initiator (0.6 mmol) were added to the flask. Subsequently, the reaction system was heated to 80 °C to obtain a matrix via in situ free radical polymerization for 6 h (under N_2). Finally, the reaction products were washed with ethanol and dried under vacuum for 48 h to obtain the PMA_{14}-3GO nanohybrid PPD. In the same manner, the different qualities (GO 6 mg; GO 9 mg) of PMA_{14}-GO nanohybrid PPDs were synthesized as above.

2.3. Cold flow property measurements

CFPP and SP are crucial indexes of the cold flow properties of diesel [17,18]. CFPP is a temperature at which a fuel is no longer filterable within a specified time limit [19]. SP is the highest temperature at which the diesel sample loses its fluidity [20]. In this study, the CFPP and SP of the diesel samples were measured on a SYP2-2 multi-functional low-temperature tester (Shanghai Boli Instrument Co., Ltd., China) in accordance with ASTM D2500 and GB 19,147, respectively. The CFPP and SP values of each diesel sample were measured thrice, and the final results were averaged.

2.4. Other fuel property measurements

Other fuel properties are also critical indicators for cold flow properties of diesel fuel. Each of the three PMA_{14}-GO nanohybrid PPDs was added to diesel at 0.03%, 0.05%, 0.07%, 0.1%, 0.15%, 0.2%, and 0.25% (wt) levels. These properties were analyzed according to the standard methods, such as ASTM D664 for AV (mg KOH/g), ASTM D93 for FP (°C), ASTM D7545 for OS (h, 110 °C), and ASTM D445 for υ (40 °C, mm^2/s).

All diesel samples were evaluated in triplicates to ensure the accuracy of the experimental data. Final results were averaged and are displayed in the table.

2.5. Viscosity measurements

Viscosity, the most important rheological parameter, strongly influences the cold flow properties of diesel fuel [21,22]. However, temperature also strongly influences viscosity. The viscosity–-temperature curves of the diesel samples were measured by an advanced rheometer (Anton Paar MCR302) with a shear rate of $5\ s^{-1}$ at a temperature ranging from 20 °C to −30 °C [23].

2.6. Polarizing optical microscopy (POM) measurements

The wax crystals morphology of the diesel samples was observed by using a DM2500P polarizing optical microscopy (Leica, Germany) under the conditions: a given cooling rate of 0.8 °C/min, and the micrograph was took at 1 °C intervals under a 100× magnification.

2.7. Differential scanning calorimetry (DSC) measurements

The DSC curves of the diesel samples were recorded by using Q2000 differential scanning calorimetry (TA Instruments, America) to observe the wax crystal morphology. An 8–10 mg diesel samples were tested at a scanning rate of 5 °C/min from 30 to −50 °C.

2.8. Emission performances measurements

A 2.5 L turbocharged fourcylinder indirect injection (IDI) diesel engine was used to test the emission performances. Specifically, the exhaust gas emissions carbon monoxide (CO), carbon dioxide (CO_2),