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Submicron carbon-based hybrid nano-pour-point

and excellent viscosity depressant

depressant with outstanding pour point depressant

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# **KEYWORDS**

Graphene oxide; Carbon nanospheres; Oxidized carbon nanotubes; Depressant; Depression mechanism Abstract We have investigated the effective utilization potential of carbon nanomaterials in the field of pour point depressants, and reported three kind of carbon-based hybrid nano-pour-point depressants with different dimensions. In this paper,  $poly-\alpha$ -olefins-acrylate high-carbon ester pour point depressant (PAA-18) was prepared by esterification and polymerization as the basic pour point depressant. Then, the basic pour point depressant PAA18 was modified by solvothermal method with graphene oxide (GO), carbon nanospheres (Cna) and carbon nanotubes (OCNTs). The morphology and structure of the composites were analyzed by SEM, FTIR and XRD. The results showed that PAA18 was successfully in situ polymerized on GO, Cna and OCNTs. We took the simulated oil as the experimental object, and evaluated its pour point, rheological properties and wax crystal morphology, and achieved excellent results. In the three carbon-based hybrid nanopour-point depressants with different carbon contents, the oxidation carbon nanotubes composite pour point depressant (PAA18-1 % OCNTs) with carbon content of 1 % had the best pour point and viscosity reduction effect when the dosage was 1250 ppm, which could make the pour point of the simulated oil containing wax decrease by 16 °C. PAA18-1 % OCNTs reduced the pour point by 5 °C more than PAA18. This paper provides reference for the application of carbon nanomaterials in the field of pour point depressant.

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#### 1. Introduction

Wax-based crude oil has the characteristics of high pour point, high viscosity, high wax content and poor low temperature fluidity (Lg et al., 2021; Yang et al., 2021). This will not only seriously increase the power and thermal energy consumption of pipeline crude oil, but also bring great challenges to crude oil exploitation, transportation, processing and storage (Li et al., 2020; Cao et al., 2021). In order to solve this problem, nanomaterials are widely used in the field of pour point depressants because of their excellent thermal and mechanical properties (Yao et al., 2018; Yang et al., 2017; Li et al., 2018).

In recent years, researchers have used this characteristic of nanomaterials to combine them with polymers to improve their thermal and mechanical properties, so as to broaden the application range of polymers (Nurfajrin et al., 2021). It is found that nanomaterials have unique characteristics of molecular size and large specific surface area. Combining nanomaterials with pour point depressants can effectively affect the thermal deformation temperature, crystallinity, crystallization rate and grain size of wax crystals, which not only makes the pour point depressant effect of polymers more prominent, but also injects a new power source for the development of pour point depressants (Sun et al., 2017; Wu et al., 2012; Shao et al., 2010).

Most traditional pour point depressants are composed of polar and non-polar parts. Long-chain alkyls are usually non-polar parts that can co-crystallize and adsorb wax crystals (Wang et al., 2020; Steckel et al., 2022; Mka et al., 2022). The polar part blocks the growth of wax crystals and the formation of three-dimensional network structure (Atta et al., 2011; Cao et al., 2013; Hashemi et al., 2014). Deka B et al. (Barasha et al., 2018) polymerized triethanolamine into trimer, and then reacted with oleic acid to form tri-triethanolamine dioleate. The experimental results show that the pour point depressant can effectively improve the low temperature rheological properties of crude oil and reduce the pour point of crude oil by 17 °C. Admiral A et al. (Admiral et al., 2016) prepared emulsified acrylate polymer, verified that the pour point reduction effect of emulsified acrylate was significantly higher than that of acrylate, and the pour point of crude oil was reduced by about 12 °C. The flow ability of emulsified PD90 possesses higher kinetic energy so that it could efficiently move around freely and then propagate to the waxes molecule in order to inhibit the crystallization growth of paraffin wax. The fundamental reason is that the flow ability of emulsified acrylate has high kinetic energy, which can be effectively and freely transferred to wax molecules to inhibit the crystallization growth of wax.

With the continuous exploration of pour point depressant by a large number of researchers, it is found that the excellent thermal and mechanical properties of nanomaterials can be used to combine with polymers to improve the thermal and mechanical properties of polymers, so as to broaden the application range of polymers (Binks et al., 2015; Kazantsev et al., 2021; Zhang et al., 2021, 2020). Carbon nanomaterials have also been widely used in the oil industry, such as demulsification of crude oil emulsion (Huang et al., 2019; Hxa et al., 2019; Ye et al., 2019), treatment of oily wastewater (Jlddt et al., 2020), and analysis of reservoir tracers (Wang et al., 2011). In recent years, they have also been applied in the field of pour point depressants. Among various nanoparticles, graphene oxide (GO) is material with unique single-layer two-dimensional honeycomb lattice structure due to its high chemical inertness, high stability and high mechanical strength, which has attracted wide attention in the field of oilfield chemistry (Coussirat et al., 2019; Gu et al., 2012). Iman Jaberi et al. (Jaberi et al., 2020) synthesized GO-PEG nano-composite pour point depressant by functionalization reaction of graphene oxide and polyethylene glycol (PEG). GO-PEG nano-structure was added into crude oil with different concentrations of 100, 200, 400, 800 and 1000 ppm. The oil pour point, wax appearance temperature, viscosity and oil deposition rate of each sample were detected. The results showed that the addition of GO significantly reduced the pour point of oil, and the temperature can be reduced from 17 °C to -5 °C. Rohit Sharma et al.

(Sharma et al., 2019) synthesized nanocomposite pour point depressants with different contents of graphene oxide (GO) and copolymer polymethyl methacrylate (PMMA) by in-situ free radical polymerization. The experimental results showed that the thermal stability of the synthesized nanocomposites was better than that of PMMA, and the pour point of crude oil was reduced by 23 °C and the apparent viscosity was reduced by 99.8 % by the nanocomposites with 1 % graphene content, which was obviously better than that of PMMA. Zhao et al. (Zhao et al., 2018) prepared a novel nano hybrid polytetradecyl methacrylate graphene oxide (PMA14-GO) pour point depressant (PPD) by in-situ radical polymerization using graphene oxide as raw material. The results showed that the new nano hybrid pour point depressant was better than the tetradecvl methacrylate pour point depressant. At the same time, many researchers have found that graphene, carbon nanospheres (Cna) and carbon nanotubes (CNTs) are carbon-based nanomaterials with different dimensions, and carbon nanospheres not only have high chemical inertness, high stability, and high mechanical strength of graphene, but also endow carbon nanospheres with high density, high strength, and high specific surface area due to their unique structure (Wang et al., 2021; Wang et al., 2022). Carbon nanotubes with high surface energy, high stability, high specific surface area, known as one of the highest melting point materials (Ali et al., 2019; Zhang and Xie, 2021; Xla et al., 2020). At present, although graphene has been deeply studied and explored in the field of pour point depressants (Du et al., 2010; Mohamadian et al., 2020; Alemi et al., 2021), carbon nanospheres and carbon nanotubes have not been applied. Therefore, carbon nanospheres and carbon nanotubes are introduced into traditional pour point depressants in this paper.

In this paper, three carbon-based nanomaterials with different dimensions were used to modify the traditional polymer pour point depressant. The advantages of eutectic interaction between traditional polymer pour point depressant and wax crystal are effectively combined with those of three carbon materials. Graphene oxide composite pour point depressant, carbon nanosphere composite pour point depressant and carbon nanotubes composite pour point depressant were prepared, and their structures and properties were characterized. The wax-containing simulated oil was taken as the object to evaluate the pour point, rheological property and wax crystal morphology, and finally the depression mechanism was discussed in depth. The application of carbon nanomaterials in the field of pour point depressant not only broadens the application range of carbon nanomaterials, but also provides a new idea for the application of efficient pour point depressant.

#### 2. Experiment

#### 2.1. Materials

1-octadecylamine, oil amine, multi-walled carbon nanotubes (MWCNT) were purchased from Shanghai McLin Biochemical Technology Co., ltd.; acrylic acid and 1-octadecanol were purchased from China Pharmaceutical Group Chemical Testing Co., ltd.; tert-butyl benzoyl peroxide was purchased from Taizhou Dingfa Chemical Co., ltd.; azodiisobutyronitrile, xylene and H<sub>2</sub>O<sub>2</sub> were purchased from Nanjing Chemical Reagent Co., ltd.; hydroquinone purchased in Tianjin Taixing reagent factory; methanol was purchased from Tianjin Fuchen Chemical Preparation Plant; graphene was purchased from Shenzhen Suiheng Technology Co., ltd.; concentrated sulfuric acid was purchased from Yantai Far East Fine Chemical Co.. ltd.; potassium permanganate was purchased from Jintan Experimental Factory, Shanghai Chemical Research Factory; sodium nitrate and glucose purchased were purchased from Tianjin Kaitong Chemical reagent Co., ltd.; anhydrous

ethanol, potassium persulfate (KPS), potassium hydroxide (KOH) were purchased from Tianjin Tianli Chemical reagent Co., ltd.; paraffin balls were purchased from Henan Xinwei Equipment Co., ltd.; -20 diesel oil was purchased from Nanjing Jingying Petrochemical Co., ltd. The purity of the above experimental materials are analytical pure grade. The waxy crude oil came from a block in Daqing Oilfield. Its wax content is as high as 18.1 % pour point as 34 °C. The physiochemical characteristics are shown in Table 1.

Petroleum products pour point tester, SYD-510G, Shanghai Changji Geological Instrument Co., ltd.; modular intelligent advanced rheometer, MCR, Andongpa (Shanghai) Business Co., ltd.

# 2.2. Synthesis of basic pour point depressant

#### 2.2.1. Synthesis of basic pour point depressant

Preparation of octadecyl acrylate: put quantitative octadecanol, solvent xylene and polymer inhibitor hydroquinone into three flasks with thermometers, condenser tubes and electric mixers. Dissolve octadecanol completely by stirring and heating to 55 °C. Then 25 ml acrylic acid and tertbutyl benzoyl peroxide were rapidly added to the flask, the stirring rate was adjusted to about 400 r/min, and the temperature was slowly increased to 100 °C. After a period of heat preservation, the temperature gradually increased to 100-130 °C, and the stirring reaction was increased to 550 r/min. The heating reflux was about 5 h, and the reaction stopped when the water quantity of the separator below the condenser reached the theoretical value. After the reaction, xylene and excess acrylic acid in the reaction product were extracted by vacuum distillation immediately. Octadecyl acrylate was obtained by vacuum drying in a constant temperature drying oven at 40 °C for 24 h.

Preparation of poly-α-olefin-carbon acrylate pour point depressant (PAA18): The flask containing octadecyl acrylate, a-octadecyl olefin and solvent xylene was placed in an oil bath, and the high-speed agitator and nitrogen pipe were installed. A certain amount of azobisisobutyronitrile was used as initiator for free radical polymerization. Replacing the air in the flask with nitrogen purge and slowly dropped the initiator azobisisobutyronitrile solution when heated to 70 °C by high speed stirring. When the temperature was slowly raised to 85 °C -100 °C, the stirring rate was kept at 500 r/min, the polymerization was finished after 6 h, and the reactant was poured out. When the solution was cooled to room temperature, it was poured into the beaker, and 50 ml methanol was added to purify the polymer. The precipitate was taken out and dried in a constant temperature drying oven at 40 °C for 24 h in vacuum to obtain poly-α-olefin-carbon acrylate pour point depressant (PAA18). Synthesis route of PAA18 is shown in Fig. 1.

# 2.2.2. Pretreatment of carbon materials

### (1) Preparation of graphene oxide.

The preparation process of graphene (GR) treated by Hummer method is shown in S1.

(2) Preparation of carbon nanospheres.

Carbon nanospheres were prepared by mature glucose hydrolysis technology, and the preparation process is shown in S2.

(3) Preparation of oxidized carbon nanotubes.

The oxidation process of S3 carbon nanotubes is shown in S3.

### 2.2.3. Synthesis of carbon-based hybrid nano-depressant

Different amounts of graphene oxide (GO), carbon nanospheres and carbon nanotubes (O-CNTs) were added to 40 ml xylene, and the suspension was ultrasonically treated at low temperature (less than 5 °C) for 30 min to make it uniformly dispersed. Then PAA18 (80 wt%) was added into the uniform dispersions of the three carbon materials to form the mixed solutions of 0.5 %, 1 %, and 1.5 % poly- $\alpha$ olefins-high carbon acrylate and carbon materials. The mixed solution was poured into the reactor and purged with nitrogen for 10 min. After exhausting the air in the reactor, it was sealed and placed in a muffle furnace. The reaction was held at 100 °C for 7 h. After the reaction was cooled to room temperature, 40 ml methanol was added to initiate precipitation, and the precipitation product was dried in an electrothermal constant temperature drying oven at 80 °C for 12 h to obtain graphene oxide composite pour point depressant, carbon nanospheres composite pour point depressant and carbon nanotubes composite pour point depressant. The preparation process is shown in Fig. 2.

### 2.3. Preparation of wax-containing simulated oil

60 g paraffin balls were put into 500 ml flask and 340 g -20 diesel was added as solvent oil. The flask was placed in 75 °C water bath and stirred at 500 r/min for 6 h, so that paraffin and diesel were fully mixed and cooled to room temperature.

#### 2.4. Performance test and characterization

#### (1) Scanning electron microscopy.

The structure and apparent morphology of carbonbased hybrid nano-depressant were measured by scanning electron microscope (Quanta 250 FEG). The dispersed samples were dropped on the copper sheet, and the samples were bonded to the conductive tape on the sample seat after drying.

Table 1	Basic physical properties of waxy crude oil produced in a block of Daqing Oilfield.									
Density kg·m <sup>-3</sup>	Dynamic viscosity (50 °C) mPa·s	Gum %	Asphaltene %	Wax content %	Pour point °C					
943.0	180.2	22.98	12.75	18.1	34					



R1 and R represent alkyl chains with carbon numbers of 15 and 18, respectively

Fig. 1 Synthesis route of poly-α-olefin-high-carbon acrylate pour point depressant.



Fig. 2 Synthesis of carbon-based hybrid nano-depressant.

(2) FT-IR spectroscopic analysis.

The functional groups of carbon-based hybrid nano-depressant were determined by Fourier transform infrared spectrometer. The specific experimental operation was as follows: graphene oxide and composite samples were mixed with potassium bromide at a ratio of 1: 100 and grinded evenly in the bowl, and pressed into an infrared spectrometer for detection. The scanning times were 64, and the wavelength range was  $500 \sim 4000 \text{ cm}^{-1}$ .

(3) X-ray diffraction analysis.

The carbon-based hybrid nano-pour-point depressant was analyzed by XRD (XPert Pro). With CuKa as the target source, the scanning range was set to $2\theta = 5 \sim 70^{\circ}$ .

#### (4) Determination of pour point.

According to the petroleum and natural gas industry standard of the People's Republic of China (SY/T 0541– 2009) crude oil pour point determination method, the pour point of Daqing crude oil, wax-containing simulated oil and treated oil were determined. Firstly, the sample oil is placed in a water bath at 70 °C for 2 h, until the sample oil is uniform and has good fluidity to eliminate the thermal history and shear history. The quantitative pour point depressant was added to the crude oil with a micro-liquid shifter, and the mixture was stirred evenly and kept for 30 min. Then prepare the round-bottom glass test tube and the round-bottom glass casing, pour the sample into the boundary of the round-bottom

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glass test tube (cut an annular marking at the outer wall of the test tube 50 mm  $\pm$  3 mm from the bottom of the tube), and quickly insert the thermometer. The glass casing with samples was moved smoothly and quickly to the pour point tester of petroleum products, and the temperature of the equipment was adjusted to 0 °C, so that the cooling temperature was controlled as far as possible at 0.5 °C / min. When the sample oil temperature drops 2 °C, take out the test tube slightly tilted and observe (take out the observation to put back operation should remain within 3 s). When the liquid level of the sample does not move, the test tube is immediately removed and placed horizontally for 5 s, and the oil is condensed when there is no displacement. In order to ensure the accuracy of the experiment, the same sample needs to be measured repeatedly, and the error of the measurement results is within 2 °C.

(5) Determination of rheological properties.

MCR series modular intelligent advanced rheometer was used to determine the rheological properties of waxcontaining simulated oil without additives and waxcontaining simulated oil treated with different dosages of pour point depressants. The initial temperature of the experiment was set at 30 °C and sheared at constant temperature of 30 °C.

(6) Determination of wax crystal morphology.

Polarized microscope equipped with camera was used to determine and analyze the wax crystal morphology of waxcontaining simulated oil without additives and waxcontaining simulated oil modified with different dosages of pour point depressants. The sample was moved to the glass slide with a drop tube and placed in the loading table. The wax crystal morphology of the sample was observed when the sample was cooled to 15 °C at a cooling rate of 1 °C/min.

# 3. Results and discussion

### 3.1. Structure and property characterization

# 3.1.1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis

The size of graphene oxide, carbon nanospheres and carbon nanotubes, and the morphology of graphene oxide composite pour point depressant (PAA18-1 % GO) with 1 % carbon content, carbon nanospheres composite pour point depressant (PAA18-1 % Cna) with 1 % carbon content and carbon nanotubes composite pour point depressant (PAA18-1 % OCNTs) with 1 % carbon content were tested by SEM and TEM. The results are shown in Fig. 3.

Fig. 2 (a) shows that graphene oxide is irregular and thin layered structure with different sizes. There are many folds in the single layer, and the edges are smooth. Layers overlap with each other. Organic molecules exist between layers through electrostatic interaction. Interestingly, as shown in Fig. 2(b), it is found that the layered structure of graphene has been combined with the poly- $\alpha$ -olefins-*co*-glycol acrylate pour point depressant, showing a thick layered structure as a whole. The layers adhere to each other, showing irregular morphology and some flake and block structures attached to the layered structure, indicating that the graphene oxide aggregates have been densely dispersed on the skeleton of the polymer. Fig. 2(c) shows that the carbon nanospheres have uniform and regular spherical structure, smooth edge and no pit-like defects. From 2(d), it can be observed that the composite materials are in irregular spherical arrangement, and the particle size is larger than that of the carbon nanospheres. We are surprised to find that there are uniform block attachments on the surface of the carbon nanospheres (as shown in Fig. 2(d) embedding figure), which are the free radical polymerization products between Cna and PAA18. Fig. 2(e) shows that the oxidized carbon nanotubes (OCNTs) are cylindrical structures, showing a transparent tubular structure as a whole. The appearance is round and smooth, and they are intertwined with each other. Through Fig. 2(f) and the embedded partial amplification diagram, we can clearly see that poly- $\alpha$ -olefinsacrylic acid high-carbon alcohol ester pour point depressant (PAA18) is free radical polymerized on the oxidized carbon nanotubes.

Through morphology analysis, we can preliminarily see that the three kinds of nanocomposite pour point depressants have been successfully prepared, and the structure and morphology of the nanocomposite pour point depressants retain the structure of raw materials graphene oxide (GO), carbon nanospheres (Cna) and carbon nanotubes oxide (OCNTs), and there is a big difference at the same time. It can be seen that different structural appearance of particles may represent different physical and chemical properties. The geometric shape and dispersion state of nanoparticles in the polymer matrix and the interaction between particles and polymer chains determine the structure and properties of nanocomposites. Solvothermal method can not only change the size of the crystal, but also change its apparent morphology (Venugopal et al., 2012; Du et al., 2010).

# 3.1.2. Fourier transform infrared spectroscopy (FT-IR) a nalysis

The functional groups of the basic pour point depressant, graphene oxide, carbon nanospheres, carbon nanotubes and graphene oxide composite pour point depressant (PAA18-1 % GO), carbon nanospheres composite pour point depressant (PAA18-1 % Cna) and carbon nanotubes composite pour point depressant (PAA18-1 % OCNTs) with carbon content of 1 % were tested by Fourier infrared spectrometer, and the synthesis results of the composite pour point depressant were further discussed as shown in Fig. 4.

It can be observed from Fig. 4 that PAA18 had no double bond stretching vibration absorption peak, indicating that the pour point depressant had become polymer from monomer. completed the transformation from monomer to polymer. Among them, the non-cyclic ester carbonyl stretching vibration absorption peak at 1727 cm<sup>-1</sup>, the  $-[CH_2] - (n \ge 4)$ in-plane rolling vibration absorption peak at 716  $\rm cm^{-1}$ , the in-plane bending vibration absorption peak at 1163  $\text{cm}^{-1}$ , and the stretching vibration absorption peaks of C-H bond at 2922  $\text{cm}^{-1}$  and 2854  $\text{cm}^{-1}$  were all the characteristic peaks of the synthesized basic pour point depressant. And we found that ester carbonyl absorption peak and C-H bond absorption peak was more obvious, which was due to its large dipole moment, resulting in strong absorption. We found that in addition to the absorption peaks caused by C=C stretching vibration at 1618 cm<sup>-1</sup> and graphene characteristic absorption peaks caused by carbon skeleton vibration at 1388 cm<sup>-1</sup>, there were also strong characteristic absorption peaks of 1713 cm<sup>-1</sup> carbonyl group, O-H in-plane deformation stretching vibration absorption peaks at 1218 cm<sup>-1</sup>, and epoxy C–O charac-



Fig. 3 Morphology of Carbon Materials and Composites (a) GO (b) Cna (c) OCNTs (d) PAA18-GO (e) PAA18-Cna (f) PAA18-OCNTs.



Fig. 4 FI-IR of Carbon Materials and Composites.

teristic stretching vibration absorption peaks at 1058 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> in the characteristic curve of GO. This was because many characteristic oxygen-containing groups appeard in the oxidation process of graphene, such as -COOH, -OH, -C=O, etc. (Fujii et al., 2020). At the same time, we can observe the characteristic peaks of the infrared curve of carbon spheres were as follows: the stretching vibration broadening peak of hydroxyl at 3411 cm<sup>-1</sup>, the stretching vibration peak of C=O in aromatic ring at 1700 cm<sup>-1</sup>, the in-plane stretching vibration peak of C=O in aromatic ring at 1605 cm<sup>-1</sup>, the bending vibration peak of aromatic hydroxyl at 3028 cm<sup>-1</sup>, and the out-of-plane bending vibration peak of aromatic

hydrocarbon C-H at 784 cm<sup>-1</sup>. The key to the synthesis of carbon spheres was the emergence of aromatic rings, which indicated that glucose undergoes hydrolysis and aromatization in the hydrothermal process (Wang and Liu, 2014). Moreover, we found the stretching vibration peak of -C=C- at 1604 cm<sup>-1</sup>, the stretching vibration characteristic broad peak of hydroxyl at 3465 cm<sup>-1</sup>, and the bending vibration absorption peak of ester base at 1163  $\text{cm}^{-1}$ . This was because there were many characteristic oxygen-containing groups in the oxidation process of CNTs. The experimental results showed that the curve trend of PAA18 did not change significantly after the addition of carbon materials. This was because the addition of carbon materials was small, and the composite pour point depressant was based on PAA18. We found that the infrared curve of the composite pour point depressant included not only the characteristic strong peaks of the basic pour point depressant, but also the characteristic strong peaks of the carbon nanospheres, indicating that the three carbon-based hybrid nano-pour-point depressants were successfully prepared.

# 3.1.3. X-ray diffraction (XRD) analysis

The crystallinity of basic pour point depressant PAA18, carbon materials and carbon-based hybrid nano-depressant with 1 % carbon content were tested and analyzed by X-ray diffractometer, and the synthesis of composite pour point depressant was further discussed. The XRD spectrum is shown in Fig. 5.

At present, it is recognized that the strong diffraction peaks of graphene (GR) and carbon nanotubes (CNTs) should be around 23° and 26.4°. However, the diffraction peaks of GO and OCNTs measured in this study shift to the left, which were located at 12.43° and 25.89°, respectively. It was found that the cell parameters of the two composites increased and the crystal plane spacing d increased through the calculation



Fig. 5 XRD patterns of composites.

of Braggs equation (Li et al., 2013). This was due to the adhesion of hydroxyl, carbonyl and epoxy groups on the surface and edge of CNTs, which can prove that graphene and CNTs have been completely oxidized. It was also observed from Fig. 4 that the characteristic peaks of PAA18 at 8.59° and 39.78° and the characteristic peaks of GO at 42.36° could correspond to the diffraction peaks of PAA18-1 % GO, respectively. At the same time, the characteristic peak of 12.43° corresponding to GO disappeared in the composite, while the diffraction peak of PAA18 at 22.36° disappeared and shifted to the left, about 0.81°, and a strong and wide characteristic peak appeared at 21.55°. A prominent hump appeared in the carbon nanospheres, and the diffraction peaks of PAA18-1 % Cna correspond to PAA18 and Cna at  $2\theta$  = 8.59° and 21.51°, respectively. It was found from Fig. 4 that the characteristic absorption peaks of OCNTs with different intensities appeared at 25.89°, 42.38°, 44.44° and 51.61°, mainly corresponding to the (002), (013), (013) and (016) crystal planes of the carbon nanotube structure, which can be found in the characteristic peaks of PAA18-1 % OCNTs, and the diffraction peak of PAA18-1 % OCNTs contains the diffraction peak of PAA18 at 8.59°. In this study, the broadening, moving and strengthening of the diffraction peaks were due to the preferential growth orientation of the carbon material due to its high surface activity during the free radical polymerization of carbon material and PAA18, which made the polymer adhere to the carbon material to form a coating process without damaging the crystal structure. At the same time, it was found through calculation that the spacing of PAA18-1 % GO, PAA18-1 % Cna and PAA18-1 % OCNTs after polymer grafting was further increased, which confirmed that the three carbon materials experienced the recrystallization growth process in the solvothermal preparation of composites, and the adhesion of PAA18 groups on the surface and edge of carbon materials. From the XRD curve diffraction peak shape of Fig. 5, the peak width and sharp, indicating that PAA18-1 % GO, PAA18-1 % Cna and PAA18-1 % OCNTs composites were successfully prepared, and had the characteristics of small grain, good crystallinity and high crystalline phase content.

#### 3.2. Effect evaluation of pour point depressant.

# 3.2.1. Effect of pour point depressant on wax-containing simulated oil pour point

The effects of basic pour point depressant PAA18 and carbon-based hybrid nano-pour-point depressants with different carbon contents on wax-containing simulated oil pour point were mainly studied, and the results are shown in Fig. 6.

Fig. 6 and Table 2 showed that the pour point of the blank wax-containing simulated oil is 30 °C, and the pour point of the simulated oil decreased gradually with the increased of the dosage of the pour point depressant, and the trend was the same. It showed that the low temperature fluidity of the oil can be improved by PAA18 basic pour point depressant and carbon-based hybrid nano-pour-point depressant with different carbon content, and the dosage of the pour point depressant can significantly affect the pour point depressant effect. From Fig. 5, it can be found that adding 1250 ppm PAA18 can reduce the pour point of wax-containing simulated oil from 30 °C to 19 °C, and the decrease was 11 °C. Among the graphene oxide composite pour point depressants, PAA18-1 % GO had the best pour point depressant effect at the dosage of 1250 ppm, which can reduce the pour point of wax-containing simulated oil to 15 °C and further reduced 4 °C on the basis of PAA18 pour point depressant. In the carbon nanospheres composite pour point depressant, when the dosage was 1000 ppm and 1250 ppm, PAA18-0.5 % Cna can make wax simulated oil pour point dropped 13 °C, 2 °C more than PAA18. In the composite pour point depressant of oxidized carbon nanotubes, we find that the pour point of simulated oil containing wax can be reduced by 16 °C at the dosage of 1250 ppm and 5 °C on the basis of PAA18 pour point depressant, which improved the low temperature fluidity of waxy crude oil best. When the dosage is less than 1000 ppm, GO provides nucleation sites on the surface of wax molecules and produces adsorption. The wax crystal is adsorbed on the nanoparticles and maintains a dense morphology, so it has good pour point depressant effect. However, when the dosage is more than 1000 ppm, it may produce self-gelation phenomenon, which makes the solubility of some pour point depressants worse, thus affecting the pour point depressant



Fig. 6 Pour point of simulated oil containing wax.

Table 2	Pour point of simulated oil containing wax.									
Dosage/ Sample	PAA18	PAA18- 0.5 %GO	PAA18- 1 %GO	PAA18- 1.5 %GO	PAA18- 0.5 %Cna	PAA18- 1 %Cna	PAA18- 1.5 %Cna	PAA18- 0.5 % OCNTs	PAA18- 1 %OCNTs	PAA18- 1.5 % OCNTs
0	30	30	30	30	30	30	30	30	30	30
250	26	26	21	24	24	24	26	25	23	25
500	25	24	20	23	24	23	25	23	22	24
750	25	24	17	22	21	23	23	23	20	24
1000	21	19	16	20	17	20	21	18	16	18
1250	19	18	15	17	17	18	19	17	14	18
1500	20	18	17	20	18	19	19	17	17	19

effect of GO composite pour point depressant. Different pour point depressants have different pour point depressant effects and the optimal dosage is also different. At the same time, the solubility of carbon nanotube composite pour point depressant may be better than that of graphene oxide composite pour point depressant, so the above phenomenon occurs. It was worth noting, however, that when the dosage reached 1500 ppm, there was a certain rebound in the pour point of the simulated oil containing wax, which may be due to the excess dosage of the pour point depressant, which increased the volume of the pour point depressant molecule or carbon material and leaded to self-aggregation, making it partially ineffective or difficult to dissolve in the oil, thereby affecting the improvement of the low temperature fluidity of crude oil. In short, the addition of three kinds of carbon materials can improve the pour point depressant effect to a certain extent, and have a good synergistic effect with the traditional polymer pour point depressant (PAA18). The synergistic effect of carbon nanotubes composite pour point depressant is better than that of graphene oxide nanocomposite pour point depressant and carbon nanospheres composite pour point depressant.

# 3.2.2. Effect of pour point depressant on rheological properties of wax-containing simulated oil

In order to explore the effect of carbon-based nanohybrid pour point depressant on the rheological properties of oil products, the flow behavior of wax-containing simulated oil treated with carbon-based nanohybrid pour point depressants with different carbon contents in the range of  $0-500 \text{ s}^{-1}$  shear rate was studied under the optimal dosage of 1250 ppm at 30 °C. The results are shown in Fig. 7.

It can be observed in Fig. 6 that the viscosity trend of waxcontaining simulated oil decreased with the increase of shear rate, and the viscosity reduction rate of simulated oil showed the shear dilution behavior of non-Newtonian fluid from large to small. The results showed that when the shear rate reached a certain value, the viscosity changed little and the trend tended to be stable. It can be seen from the flow chart 7 (a) that when the shear rate reached 400 s<sup>-1</sup>, the viscosity of the oil tended to be stable. PAA18 basic pour point depressant can reduce the viscosity of wax-containing simulated oil from 31.8 mPa·s to 7.7 mPa·s, and the viscosity reduction rate was 75.8 %. The viscosity of simulated waxy oil treated with PAA18-0.5 % GO, PAA18-1 % GO and PAA18 – 1.5 % GO composite pour point depressants decreased from 31.8 mPa·s to 4.1 mPa·s, 2.8 mPa·s and 4.7 mPa·s, respectively, and the viscosity reduction rates were 87.1 %, 91.2 % and 85.2 %, respectively. From Fig. 7(b), it can be observed that the viscosity of simulated waxy oil treated with PAA18-0.5 % Cna, PAA18-1 % Cna and PAA18-1.5 % Cna pour point depressants was 5.7 mPa-s, 6.9 mPa s and 7.2 mPa s, and the viscosity reduction rates were 82.1 %, 78.3 % and 77.4 %. Fig. 7(c) showed that PAA18-0.5 % CNTs, PAA18-1 % CNTs and PAA18-1.5 % CNTs pour point depressants can reduce the viscosity of waxcontaining simulated oil to 4.3 mPa s, 2.5 mPa s and 3.7 mPa s, and the viscosity reduction rate was 86.5 %, 92.1 % and 88.4 %. Among them, PAA18-1 % CNTs pour point depressant had the largest reduction in crude oil viscosity, and the effect of improving the low temperature fluidity of waxy simulated oil was the best, which increased the viscosity reduction efficiency by 16.3 %. This showed that carbon-based nanohybrid pour point depressants with different carbon content can improve the low temperature fluidity of oil products, and had high sensitivity to simulated oil, and achieved good viscosity reduction effect. Three kinds of carbon-based hybrid nanoparticles have high surface energy and become the 'new' nucleation site of wax crystal, and adsorb on the new crystal nucleus to form a relatively narrow and dense morphology, thereby reducing the interface area and reducing the surface energy, thus forming a larger gap between the disconnected structure, releasing liquid oil wrapped by wax crystal. Therefore, the viscosity of the oil drop. In summary, in terms of improving the rheological properties of oil products, the order of viscosity reduction effect is as follows: carbon nanotubes composite pour point depressant > graphene oxide composite pour point depressant > carbon nanospheres composite pour point depressant > PAA18 basic pour point depressant.

# 3.2.3. Effect of pour point depressant on wax crystal morphology of wax-containing simulated oil

In order to explore the mechanism between graphene oxide nano-depressant and oil more comprehensively, the effect of carbon-based nano-hybrid pour point depressants with different carbon content on wax crystal morphology of wax-containing simulated oil was mainly studied. Polarized microscope was used to observe the wax crystal morphology of different composite pour point depressants. The results are shown in Fig. 8.

As shown in Fig. 8 (a) and (b), it can be observed that the wax wax-containing simulated oil without pour point depressant grew irregularly in large slices. The interval of a single wax crystal was large, and it overlapped and



Fig. 7 Rheological Properties of Carbon Materials and Composites.

intersected each other to form a relatively stable threedimensional network structure, which caused the liquid oil to be wrapped in it, so that the simulated oil lost its low-temperature fluidity and obtained a pour point. With the addition of pour point depressant, we found that the number, structure and size of wax crystals changed. As shown in Fig. 8 (c), when the dosage of PAA18 reached 1250 ppm, the three-dimensional network structure gradually became loose, the number of wax crystals increased, and the wax crystals decreased significantly. Among them, the small wax crystals gradually formed a number of wax crystal aggregates, which were tree-like. This structure reduced the density of wax crystal aggregates and increased the distance, and released the liquid simulated oil trapped in the stacking of large wax crystals, which weakened the ability of wax crystals to form three-dimensional network structure, and then changed the low temperature fluidity of oil products, thereby reducing the oil pour point. Moreover, we were surprised to find that the wax crystal size of the simulated oil containing wax added with three kinds of carbon-based hybrid nano-composite pour point depressants (carbon content of 0.5 %, 1 %, 1.5 %) was larger and more dispersed

than that of the basic pour point depressant PAA18, and wax crystals were surrounded by black dots. This may be because some wax crystals were co-crystallized through traditional polymer pour point depressants, and others were wax crystals. Because carbon materials provided nucleation sites on the surface of wax molecules to produce adsorption, wax crystals were adsorbed on nanoparticles and maintained a dense morphology, and moved with its movement, thereby preventing the growth of crystal nuclei. This also leaded to good dispersion of wax crystals, thus hindering the formation of three-dimensional network structure. However, we found that the wax crystals in the wax-containing simulated oil increased and aggregated after the addition of PAA18-1.5 % GO, PAA18-1 % Cna, PAA18-1.5 % Cna, and PAA18-1.5 % OCNTs. This may be because the excessive addition of carbon materials led to the low free radical polymerization degree of carbon materials and polymers, which led to the poor pour point depressant effect. In summary, the three carbon-based hybrid nano-composite pour point depressants can change the size, number and dispersion of wax crystals to a certain extent. Among them, the wax crystal morphology is best improved by PAA18-1.5 % GO,



**Fig. 8** Optical micrographs of simulated oil containing wax (a) and (b)-blank wax-containing simulation oil, (c)-PAA18, (d)-PAA18-0.5 % GO, (e) -PAA18-1 % GO, (f) -PAA18-1.5 % GO, (g)-PAA18-0.5 % Cna, (h)-PAA18-1 % Cna, (i) -PAA18-1.5 % Cna, (j)-PAA18-1.5 % Cna, (k) -PAA18-0.5 % OCNTs, (l) -PAA18-0.5 % OCNTs.

PAA18-1 % Cna, PAA18-1.5 % Cna and PAA18-1 % OCNTs composite pour point depressants.

# 3.3. Depression mechanism

Based on the above reports, it is found that the pour point depressant effect of carbon nanotubes composite is better than that of graphene oxide composite and carbon nanospheres composite, and the ability to improve the low-temperature fluidity of oil is the strongest. This may be because: from the point of view of the structure of nanoparticles, carbon nanotubes are one-dimensional quantum materials, the tube shape is bent and the length-diameter ratio is much larger than that of graphene oxide and carbon nanospheres, and more space sites are formed between carbon nanotubes and traditional polymer pour point depressants, so that the composite degree of nanocomposites is higher (Chae, 2020). In addition, the carbon atoms in the oxidized carbon nanotubes are mainly sp<sup>2</sup> hybrid, and their special tube types can form the corresponding topological structure, which can form the sp<sup>3</sup> hybrid structure to a certain extent (Lu et al., 2015). That is to say, the oxidized carbon nanotubes are a material with both  $sp^2$  and sp<sup>3</sup> hybrid states. Compared with the free-moving  $\pi$  bonds of graphene oxide, the  $\pi$  bonds outside the graphene oxide sheet have the characteristics of highly delocalization, which can be better combined with traditional polymer pour point depressants, and the integrity of the composite nano-pour-point depressant is stronger.

In order to further explore the effect of three carbon-based nano-hybrid pour point depressants on wax crystal structure and wax crystal morphology, we carried out a preliminary study from the molecular structure and wax crystal morphology as shown in Fig. 9. According to previous reports, it can be seen that pour point depressant molecules can reduce the wax precipitation point of oil products, break the ring wax crystal surface, reduce the wax crystal size, and make the wax crystal appear in a small and dispersed form. It can be speculated that there is a eutectic mechanism between the pour point depressant molecule and the wax crystal. The long chain alkyl of the non-polar group in the pour point depressant molecule represents the crystalline phase, and the polar group ester group is used as the non-crystalline phase, which hinders the growth of the wax crystal in the X and Y directions of the lamellar crystal, and promotes the growth of the Z axis, so that the wax crystal exists in a small and dispersed form with the oil. At the same time, the presence of graphene oxide layer, carbon nanospheres and carbon nanotubes in the polymer structure increases the strength of the polar and non-polar groups, and enhances the guiding effect on the crystallization and nucleation of the wax crystal. As shown in Fig. 8, three kinds of carbon-based nanohybrids have high surface energy and become the new nucleation site of wax crystals. The wax molecules adsorb on the new crystal nucleus to form a relatively narrow and dense morphology, which reduces the interface area and reduces the surface energy, thus forming a larger gap. The liquid oil wrapped by wax crystal is released, which greatly reduces the wax-oil interface area, effectively hinders the formation of three-dimensional network structure, thereby improving the low temperature fluidity of oil and reducing the pour point of oil.



Fig. 9 Mechanism diagram of carbon-based hybrid nano-depressant.

# 4. Conclusion

We reported three kinds of carbon-based hybrid nano-pour-point depressants (PAA18-GO, PAA18-Cna, PAA18-OCNTs) with good thermal stability, high crystallinity, and excellent pour point and viscosity reduction effects. More importantly, we evaluated the effects of carbon-based hybrid nano-pour-point depressants on pour point, rheological properties, and wax crystal morphology by taking wax-containing simulated oil as the experimental object. It was found that the addition of carbon nanomaterials effectively improved the pour point reduction effect of PAA18, and the order of pour point and viscosity reduction ability was PAA18-OCNTs > PAA18-GO > PAA18-Cna > PAA18. The excellent pour point and viscosity reduction effect of oxidized carbon nanotubes is attributed to the unique tubular structure of oxidized carbon nanotubes with more spatial sites and the highly delocalization characteristics of the  $\pi$  bonds outside the graphene sheets of oxidized carbon nanotubes. In addition, we also found that the wax crystals treated by nano-composite coagulants were larger and more dispersed than those of PAA18. By analyzing the eutecticheterogeneous nucleation mechanism of the pour point depressant, it was found that some wax crystals co-crystallized with the traditional polymer pour point depressant, while the other part of the wax crystals became the new nucleation site of the wax crystals due to the high surface energy of the three carbonbased nanohybrid particles, and adsorbed on the new crystal nucleus to form a relatively narrow and dense morphology, thereby reducing the interfacial area and reducing the surface energy, thus forming a disconnected structure with larger spacing and releasing the liquid oil wrapped by the wax crystals. The application of carbon nanomaterials in the field of pour point depressant not only broadens the application range of carbon nanomaterials, but also provides a new idea for the application of efficient pour point depressant.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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