The effect of nanohybrid materials on the pour-point and viscosity depressing of waxy crude oil

WANG Feng¹, ZHANG DongMin², DING YanFen¹, ZHANG LiXin², YANG MingShu^{1*},
JIANG BaoLiang², ZHANG ShiMin¹, AI MuYang², LIU GuangWen², ZHI ShuJie²,
HUO LianFeng², OUYANG Xin² & LI Li²

¹ Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China;

² PetroChina Pipeline R & D Center, Langfang 065000, China

Received July 22, 2010; accepted August 4, 2010

The pipeline transportation of waxy crude oil is a problem both at home and abroad. In this paper, a novel nanohybrid pour-point depressant (PPD) was used to decrease the pour point and viscosity of waxy crude oil. The pour point and apparent viscosity of waxy crude oil was decreased significantly upon addition of the nanohybrid PPD, and the long-term stability of the nanohybrid PPD was superior to that of a conventional ethylene-vinyl acetate copolymer PPD. Polarized optical microscopy and X-ray diffraction were used to study the effect of the nanohybrid PPD on the crystallization of crude oil. Addition of the nanohybrid PPD reduced the amount of wax crystals, prevented their aggregation, and reduced the temperature at which the crude oil started to crystallize. The significant effect of this nanohybrid PPD on the pour point and viscosity depressing of crude oil is of great importance for facilitating the safe, efficient and energy-minimized transportation of waxy crude oil.

waxy crude oil, pour point, viscosity depressing, nanohybrid materials, crystallization

Citation: Wang F, Zhang D M, Ding Y F, et al. The effect of nanohybrid materials on the pour-point and viscosity depressing of waxy crude oil. *Chinese Sci Bull*, 2011, 56: 14–17, doi: 10.1007/s11434-010-4174-4

Crude oil is a complex hydrocarbon mixture, mainly consisting of paraffin wax, resin and asphaltene. Paraffin dissolves in crude oil at high temperature, and precipitates gradually to form paraffin wax when the temperature decreases. As the amount of paraffin wax increases, a three-dimensional network appears, leading to the loss of flowability of crude oil, which brings great difficulty to the oil exploitation and transportation. The rheology and transportation of waxy crude oil are the most important topics in the research field of oil exploitation and transportation. At present, the pipeline transportation of waxy crude oil includes both physical and chemical technology [1]. Heating transportation technology is a kind of important physical technologies, which is widely applied to transport the waxy crude oil with high viscosity and high pour point in China

especially for northeast and north china crude oil. Nevertheless, the heating transportation technology needs to consume a significant amount of fuel oil and energy, and restarting of the heating pipeline after suspension is possibly unsafe. At present, part of long-distance pipelines are operating at low transport capacity due to the deficiency of heating capacity, and by partial reverse transportation, leading to the large wastage of manpower, materials and funds.

The chemical technology associated with pipeline transportation of crude oil includes emulsification, suspension transportation and pour-point depressant (PPD) technology. Emulsification and suspension transportation technology are limited to application in water-rich areas for their large water consumption. A further disadvantage of these technologies is that subsequent dehydration of the crude oil is difficult. PPD technology improves the low temperature flowability of waxy crude oil by adding a chemical agent to

*Corresponding author (email: yms@iccas.ac.cn)

change the structure and morphology of wax crystals [2,3], and makes the wax hard to form a rigid three-dimensional network at ambient temperature. PPD technology possesses the advantages of simple operation, low cost, no requirement for post treatment, thus is convenient for automatic management of pipeline transportation, and also for offshore production and gathering transportation. Therefore, PPD technology is the simplest and most efficient method to achieve crude oil transportation at ambient or low temperature.

PPD technology was first developed in 1931, when Davis synthesized the first PPD, Paraflow, through Friedel-Crafts condensation of chlorinated paraffin with naphthalene. This kind of PPD is still widely used in lubricants. To date, a large number of crude oil PPDs have been reported [4,5], which are divided into the following categories: ethylene-vinyl acetate copolymer (EVA) and its derivatives, long chain alkyl acrylate polymer and its derivatives, styrene-maleic anhydride-long chain alkyl acrylate copolymer and its derivatives, and long chain alkyl acrylate-maleic anhydride-vinyl acetate copolymer and its derivatives. These PPDs are very effective at depressing the viscosity and pour point of crude oil, and play an important role in the pipeline transportation of waxy crude oil. However, there are still problems associated with PPD technology: (1) Particular PPDs are suited to specific kinds of crude oils, and a PPD suitable for Daqing crude oil has not been reported; (2) After complete treatment, the temperature promotion will influence the low temperature flowability of the crude oil; (3) The dynamic and static long-term stability of the treated crude oil does not satisfy the requirements for its safe transportation *via* pipeline; (4) The addition of PPDs results in the deposition of paraffin wax in the pipeline.

Because of their unique size, surface and quantum tunneling effects, nanomaterials possess prospects for application in all of the fields in the national economy. At present, in the fields of lubricants, paving asphalt, and catalysts used during processing of crude oil, nanomaterials are employed for purposes such as promoting the abrasion resistance of lubricants, and improving the stability of paving asphalt [6]. In this research, a novel kind of nanohybrid material was utilized in the field of pipeline transportation of waxy crude oil. Addition of this new PPD improves the crystallization behavior of paraffin wax in crude oil, and decreases the structural strength of crude oil at low temperature. This endows waxy crude oil with excellent low temperature flowability and long-term stability, finally allowing safe, efficient, low energy pipeline transportation of waxy crude oil to be realized.

Nanohybrid and EVA PPDs were the main materials used in this research. EVA PPDs with vinyl acetate content of 28% were dissolved in diesel fuel to give a concentration of 1 wt%. The crude oil used was a mixture of 80 wt% Daqing crude oil and 20 wt% Jidong crude oil from the Qingjing line. EVA PPD (50 g/t) was added to the waxy crude oil, and then the mixture was heated to 64°C with vigorous stirring for 5 min to obtain a homogeneous dispersion. The mixture was then slowly cooled to 25°C.

The apparent viscosity was determined in a concentric

cylinder (AR 2000ex). Generally, the shear rate of crude oil is around 20 s^{-1} during pipeline transportation, and will change according to the transport capacity and pressure. Thus the shear rate in the viscosity test was between 10 and 50 s^{-1} at 25°C. The pour point of crude oil was tested according to the standard test GB/T 510. Polarized optical microscopy (POM) was performed on an Olympus BX51 microscope equipped with an Olympus C-5050 zoom camera. The temperature was controlled using a Linkam LTS350 heating plate. Thermo X-ray diffraction (XRD) experiments were performed on an X'Pert Pro MPO (PANalytical) diffractometer using Cu K α radiation ($\lambda=1.54\text{ \AA}$), a tube voltage of 40 kV, and a tube current of 40 mA. The temperature was controlled between 55°C and 25°C with cooling rate of 0.5°C/min using a TCU2000 variable temperature stage.

To compare the viscosity depressing effects of EVA and nanohybrid PPDs, the loading of PPDs was fixed at 50 g/t; the results are shown in Table 1. The viscosity depressing effect of the EVA PPDs was obvious: the apparent viscosity decreases by about 84.7% compared with untreated crude oil at 50 s^{-1} . However, the long-term stability of the crude oil containing the EVA PPD was poor, and the decrease in the apparent viscosity deteriorated to 78.1% after the treated crude oil was preserved statically for 10 d. The viscosity depressing effect of the nanohybrid PPD was better than the EVA PPD: the apparent viscosity decreased by about 87.4% at 50 s^{-1} . The long-term stability of the crude oil containing the nanohybrid PPD was excellent; the apparent viscosity was still decreased by 85.9% compared with untreated crude oil after the treated crude oil was preserved statically for 10 d. The behavior of the treated crude oil was close to Newtonian. The pour point of crude oil is the maximum temperature at which the crude oil does not flow under fixed thermal and shear conditions. The solidification process of waxy crude oil is actually the division of liquid hydrocarbons and the freezing of crude oil when the wax changes from the dispersing state to the continuous state and the liquid hydrocarbon alters *vice versa*. Measurement of the pour point of crude oil is convenient and the equipment is simple so the pour point is generally used to roughly characterize the flowability of crude oil and monitor the variation of flowability in industry. Upon comparing the pour point data in Table 1, it was found that addition of the EVA PPD decreased the pour point of crude oil by 7.5°C. Addition of the nanohybrid PPD decreased the pour point of crude oil by almost 14.0°C, and this decrease remained stable after the sample was preserved statically for 10 d. These results are significant to industrial applications: the temperature of crude oil during pipeline transportation must be higher than the pour point, or the pipeline will become blocked. The remarkable effect of the nanohybrid PPD at decreasing the pour point of crude oil can tolerate the rapid decrease in the temperature of the crude oil when it leaves the heating station, thus saving energy during the pipeline transportation of crude oil.

The above results showed that the nanohybrid PPD de-

creases both the pour-point and viscosity of waxy crude oil significantly. Further investigations were performed to determine how the incorporation of nanohybrid PPDs changed

the crystal structure and crystallization behavior of waxy crude oil to achieve such effects.

Figure 1 shows POM images of wax crystals in crude oil.

Table 1 Comparison of the viscosity depressing effects of EVA and nanohybrid PPDs

Samples	Loading (g/t)	Time (d)	Apparent viscosity at 25°C (mPa s)					Pour point (°C)
			10 s ⁻¹	20 s ⁻¹	30 s ⁻¹	40 s ⁻¹	50 s ⁻¹	
Crude oil	0	0	4333	2420	1978	1366	771.1	30.5
Crude oil + EVA PPD	50	0	133.3	127.4	124.2	120.6	117.7	23.0
Crude oil + EVA PPD	50	10	193.8	184.3	177.8	172.4	168.6	24.5
Crude oil + nanohybrid PPD	50	0	103.1	101.4	99.8	98.4	97.2	16.5
Crude oil + nanohybrid PPD	50	10	113.5	109.2	109.6	108.8	108.8	17.0

Figure 1 POM images of paraffin wax in crude oil. (a) Crude oil samples $\times 200$; (b) crude oil samples $\times 630$; (c) crude oil + nanohybrid PPD sample $\times 200$; (d) crude oil + nanohybrid PPD sample $\times 630$.

Figure 2 Thermo XRD diffraction patterns of crude oil samples. (a) Crude oil, (b) crude oil + EVA PPD, (c) crude oil + nanohybrid PPD.

The wax crystals in the untreated crude oil were dense, the interspace between the wax crystals was small, and the wax crystals tended to agglomerate to form a three dimensional network, thus the apparent viscosity of the waxy crude oil was increased [7]. After addition of the nanohybrid PPD, the amount of wax crystals decreased, the wax crystals were sparse, and the interspace between wax crystals was wide; as a result the apparent viscosity of the crude oil treated with the nanohybrid PPD was low.

Thermo XRD provides an efficient means to characterize the effect of temperature variation on crystallization behavior [8–10]. To compare the differences in the crystallization behavior of the three samples, the samples were heated to 55°C, and subsequently cooled to 45, 35, and finally 25°C at a rate of 0.5°C/min. XRD patterns were obtained at these temperatures, as shown in Figure 2.

At 45°C, diffraction peaks appeared at 21.5° and 23.8° for both untreated crude oil and crude oil the EVA PPD, showing that these two samples began to crystallize between 55 and 45°C. Diffraction peaks appeared at 21.5° and 23.8° at 35°C in the diffraction pattern of the crude oil the nanohybrid PPD, demonstrating that this sample began to crystallize between 45 and 35°C. The temperature at which wax appeared in crude oil decreased after the addition of the nanohybrid PPD.

In conclusion, the nanohybrid PPD decreased the pour point and viscosity of waxy crude oil significantly, decreasing

the apparent viscosity of crude oil by about 87.4% at 50 s⁻¹ and the pour point by about 14.0°C. Furthermore, the long-term stability of the nanohybrid PPD was better than that of a conventional EVA PPD; the changes in apparent viscosity and pour point remained almost fixed after preserving the sample statically for 10 d. Incorporation of the nanohybrid PPD reduced the crystallization of wax in crude oil: the amount of crystals reduced, the crystals stopped aggregating, and the temperature at which wax began to crystallize decreased.

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