

Synthesis of a new type of pour point depressant and its effect on the rheological properties of model wax oil

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Abstract. Graft modification of commercial EVA PPDs to prepare new PPDs with high performance is a research hotspot in the crude oil pipelining industry. However, the acting law and mechanism of the grafted EVA PPDs were still unclear. In this paper, based on commercial EVA PPD (EVA2803), EVA-18 with side alkyl chain length 18 was synthesized by a new reaction pathway of "alcoholysis-acyl substitution". The effect of EVA on asphaltene-free model wax oil before and after modification was studied. Through a series of experiments, the influence mechanism was revealed. We believe that the eutectic effect between modified EVA PPD and paraffin determines the properties of ppd. With the increase of the length of the side alkyl chain, the eutectic effect is enhanced and the freezing point decreases to 4°C. These findings provide valuable insights into the role of alkyl side chain length in optimizing EVA-based PPD, offering promising approaches to addressing flow assurance issues in the pipeline transport of waxy crude oils.

Keywords: Modified EVA; wax oil; rheology.

1. Introduction

Oil is not only the core of global energy, but also plays a role in driving the economy and supporting industrial civilization. It penetrates every corner of life and is also the key to transportation fuel and chemical raw materials. It has dominated energy consumption for a long time and has a profound impact on national security, economic growth, and living standards [1]. At present, as the production volume of high waxy crude oil increases, when the temperature falls below the wax appearance temperature, a large number of wax crystals will precipitate in the oil phase, which will seriously affect the fluidity of waxy crude oil and bring huge problems to the extraction and pipeline transport of crude oil [2,3]. Consequently, an increasing number of researchers are focusing on the development of pour point depressants to enhance the economy and safety of waxy crude oil pipeline transportation, owing to their low dosage requirements and significant improvement in low-temperature flow properties. Ethylene-vinyl acetate (EVA) copolymer consists of a non-polar alkyl side chain and polar vinyl acetate. Due to its controllability and diversity of ratio, EVA has become the most widely commercialized polymer point-lowering agent in the world and has been widely studied by scholars in the field of the petrochemical industry [4]. With the increasing demand of high waxy crude oil pipeline transportation, traditional EVA point reduction agents have been unable to adapt to complex engineering practice, which also forces the research and development of EVA modification to become a hot spot in the field of oil and gas storage and transportation and petrochemical industry.

2. Material and Experimental

2.1 Materials

Methanol (AR), sodium hydroxide (AR), toluene (AR), triethylamine (AR), and tetrahydrofuran (AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Stearoyl chloride (AR), potassium bromide (SP), and deuterated chloroform (SP) were all sourced from Shanghai Macklin Biochemical Co., Ltd. A commercial EVA2803 PPD was obtained from Sigma-Aldrich Co., Ltd. The VA content and melt index of the EVA PPD are 28 wt% and 3, respectively.

The solute (15 wt%) in the model waxy oil comprises paraffin wax fractions with melting point ranges of 50-52°C (25 wt%) and 62-64°C (75 wt%), ensuring a carbon number distribution representative of that found in real waxy crude oil. The solvent consists of a mixture of liquid paraffin and xylene in a 3:1 mass ratio.

2.2 Synthesis of the EVA-18

The alcoholysis reaction for EVA pour point depressants was improved based on Ren's method. This process involves an ester exchange between methanol and polyvinyl acetate, modifying the polar groups of EVA. In detail, a specific mass of EVA2803 is weighed into a three-necked flask, purged with nitrogen, and equipped with a condenser. The EVA is dissolved in toluene at 80°C using a magnetic stirrer. After complete dissolution, the temperature is lowered to 45°C, and methanol (in a 1:2 molar ratio to the polar groups in EVA) is added dropwise. After 30 minutes of stirring, a 20g/L NaOH solution is added dropwise, and the reaction continues for 3 hours. The system is then cooled to room temperature, excess methanol is removed by extraction and filtration, and the product is vacuum-dried at 60°C for 12 hours to obtain EVAL [5].

EVAL is dissolved in toluene at 70°C with a 5 wt% solute concentration, under a nitrogen atmosphere and condensation reflux in a three-necked flask. Once dissolved, the temperature is lowered to 40°C, and an excess triethylamine solution is added dropwise while stirring to ensure complete dispersion and neutralization of hydrochloric acid generated during the acylation reaction. Stearoyl chloride, based on the alcoholysis rate, is weighed and dissolved in toluene (10 wt%), then added dropwise at 1-2 drops per second using a dropping funnel. The reaction is allowed to proceed for 6 hours. Afterward, excess methanol is used to precipitate the product, which is filtered and washed with deionized water to remove residual triethylamine hydrochloride. After further filtration, the graft-modified EVA (EVA-18) is obtained and vacuum-dried at 60°C for 8 hours to yield the final product.

3. Results and discussions

3.1 Pour point of model waxy oil.

Table 1 shows the change of the pour point of the model wax oil with different additives. The pour point of the blank model wax oil is 31 °C. With the pour point depressant dosage strictly controlled at 100 ppm, the addition of EVA-2 leads to a 2°C decrease in the pour point of the model waxy oil. When the length of the side alkyl chain is increased to 18, the cooling effect of EVA-18 is the best, and its pour point is reduced to 27°C.

Table 1. Pour point of model wax oil under different PPDs

Dosing condition	Pour point (°C)
Undoped	31
Doped with EVA-2	29
Doped with EVA-18	27

3.2 Yield stress test of model waxy oil

The effect of modified EVA coagulant on the yield value of model wax oil at 10 °C is shown in Figure. 1 and Table 2. It can be concluded from the experimental data that the yield stress of the blank model wax oil at 10 °C is 544.26 Pa, indicating that the model wax oil has formed a relatively strong gelling structure at this temperature. Further analysis revealed a significant decrease in the yield value of the model waxy oil, which dropped to 358.5 Pa upon the addition of EVA-2. This reduction occurred when the dosage of the pour point depressant was strictly maintained at 100 ppm. As the length of the side alkyl chain increases to 18, the yield value decreases to 280.4Pa with the

addition of EVA-18. Long alkyl side chains help to further weaken the gelling structure in the wax oil.

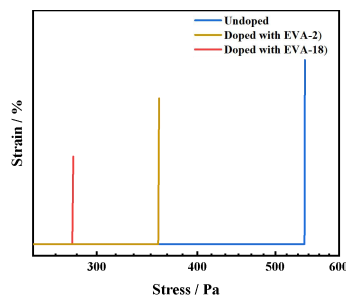


Figure. 1 Yield value of model wax at 10 °C under different dosage conditions

Table 2. Statistical table of yield value of model wax oil at 10 °C under different dosage conditions

Dosing condition	Yield stress (Pa)
Undoped	544.26
Doped with EVA-2	358.5
Doped with EVA-18	280.4

3.3 Flow curves test of model waxy oil

Figure. 1 shows the effect of modified EVA decoagulant on the flow behavior of model wax oil at 10 °C. The experimental results demonstrate that the apparent viscosity of the model waxy oil decreases significantly as the shear rate increases. This trend is observed both before and after the addition of the pour point depressant, showing typical shear-thinning behavior, where viscosity reduces with an increase in shear rate. In particular, the rheological properties of the wax oil can be improved to varying degrees after the addition of different point-reducing agents of 100 ppm. The apparent viscosity of the model wax oil is 2988.25 mPa·s when the shear rate is 100 s⁻¹. The incorporation of EVA-2 demonstrates the capacity to disassemble paraffin crystalline networks through molecular co-crystallization interactions, achieving an apparent viscosity reduction of 240.56 mPa·s in the model waxy oil system. Comparatively, EVA-18 exhibits superior performance in flow improvement efficiency, attaining the minimum recorded viscosity of 98.07 mPa·s. This substantial viscosity depression suggests that EVA-18 possesses optimized structural characteristics for paraffin crystal modification, outperforming conventional polyethylene-based additives in wax inhibition effectiveness.

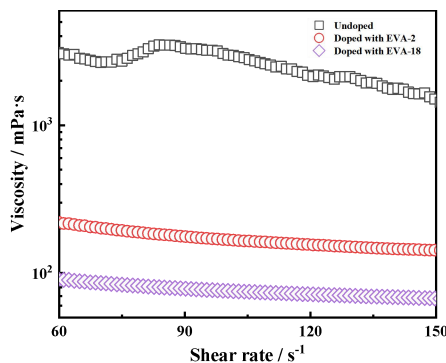


Figure. 2 Rheological curves of model wax oil at 10 °C under different dosage conditions

3.4 DSC test of model waxy oil

Figure. 1 shows the crystallization heat release curve of model wax oil without asphaltenes under different additive conditions, and Table 3 statistics the wax evolution points of oil samples under different additive conditions. Based on the experimental data, it can be concluded that the wax

appearance temperature (WAT) of the blank model waxy oil is 41.1°C. After the addition of EVA-2, the WAT of the oil sample decreases to 40.7°C, indicating that EVA-2 effectively inhibits wax precipitation to some extent. When EVA-18 is added, the wax extraction point is reduced to 40.4 °C. The pronounced paraffin inhibition originates from the elongated alkyl moieties in the engineered EVA copolymer, which establish structurally reinforced co-crystalline complexes with paraffin species under thermal quenching conditions.

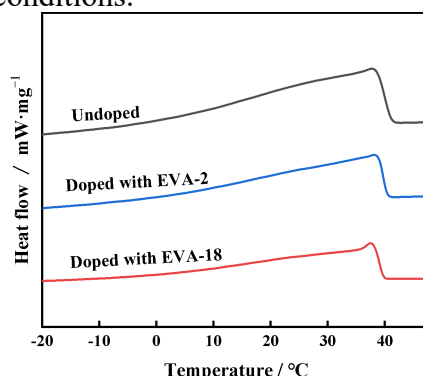


Figure. 3 Crystallization heat release curve of model wax oil with different additives

Table 3. Statistical table of wax extraction points of asphaltene-free model wax oil with different additives

Dosing condition	crystallization temperature (°C)
Undoped	41.1
Doped with EVA-2	40.7
Doped with EVA-18	40.4

4. Conclusions

In the model wax oil system, the performance of the depressant showed a significant eutectic regulatory mechanism dependence. Based on the study of modified EVA, the molecular conformation characteristics of Eva are functionally regulated by the eutectic structure formed by the polyethylene main chain and alkyl side chain. Through a series of rheological experiments and the analysis of crystallization exothermic properties, we found that the co-crystallization effect of the depressant increased with the increase of the length of the alkyl side chain. Because its side alkyl chain length is long enough, EVA-18 can fully form a stable eutectic structure with paraffin wax, showing the strongest eutectic properties. The observed molecular architecture effect demonstrates that extended alkyl substituents in polymeric additives substantially strengthen interfacial compatibility between crystallization modifiers and paraffin constituents. This structural optimization facilitates (i) steric impediment through alkyl chain-wax entanglement, and (ii) lattice matching via alkyl/wax co-crystallization behavior, synergistically enhancing the crude oil's viscoelastic response under sub-ambient conditions while maintaining optimal flow assurance parameters.

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