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The effect of a kind of hyperbranched polyester with different carbon length on flowability for crude oil

Hongping Quan[a,b,*], Liao Chen[a,b], Zhiyu Huang[a,b], Jinyu Wang[a], Cunchuan Zheng[a]

[a] College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, China
[b] Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province, Southwest Petroleum University, Chengdu, China

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ABSTRACT

In this work, using the pentaerythritol with phthalic anhydride and different long-carbon chain alcohols to synthesize a kind of hyperbranched polyester (FI) as flow improver for crude oil. The evaluation test shows FI could decline the viscosity by 65% at most on 50 °C, from 33430 mPa·s to 11670 mPa·s. Through further analyzed, TGA results confirm the designed compounds was successfully synthesized. XRD demonstrates the mixed carbon chain matched with the carbon chain distribution of saturated hydrocarbon have better ability than the single on inserting into the wax crystal. IR results indicate the reaction between the carboxyl of FI and the amino hydroxyl and hydroxyl of asphaltene and resin respectively. SEM photographs show FI react to the asphaltene and resin on the macro. In the further, the assembly model presents the FI with hyperbranched structure could increase the separation effect to improve the flowability of the crude oil.

1. Introduction

The high viscosity of crude oil makes a big trouble and deal with hardly to gather and convey [1–4]. In order to solve this question, mechanism researchers have found some theories which adsorption, co-crystallization, nucleation and improved wax solubility are widely accepted [5–10]. With decreasing temperature, the waxes generally crystallize as a kind of reticulate cubic structure and adsorb on the particles of asphaltene and resin, when the temperature of crude oil falls below the wax precipitation temperature, the aggregations of asphaltene-resin-wax would increasingly enlarge and raise the viscosity [11,12].

On the basic, some methods have been put forward to improve the low-temperature flowability. The pour point depressant (PPD) and flow improvers (FIs) which contain oil soluble long chain alkyl group and polar groups in the molecular structure are well-recognized and economically viable solution for transportation of crude oil in pipeline [13,14]. The long chain alkyl group insert into wax to disperse wax crystal, at the same time polar groups exist on the wax surface to prevent gathering, which could reduce wax crystal size. Polar moiety associated with the asphaltene and resin by dissolving and dispersing them partly which not be the “nucleation” to be adsorbed by wax [15–18].

Effects of alkyl side chain length, polar group type and content, molecular weight, oil phase composition on the efficiency of comb-like PPDs have been elucidated [19–22]. Various polymers have been used to reduce the pour point and conventional PPDs are homo- and co-polymers of different monomers [23,24]. Therefore, the high polymers have a better effect on the pour point than viscosity especially for the high-viscosity crude oil.

Till now, all the action mechanisms of PPD are based on the physical interaction between PPD and the components [25]. Based on the research, the hyperbranched and small molecular weight polyesters as flow improver were synthesized by using the pentaerythritol, phthalic anhydride and high alcohols which carbon number distribution is partly the same proportion to the n-paraffin of crude oil sample.

2. Experimental

2.1. Material

The crude oil sample used in this study was obtained from Xinjiang Oilfield, China. The reagents, pentaerythritol, phthalic anhydride, tetradecanol, hexadecanol, octadecanol, para-toluenesulfonic acid and methylbenzene were analytical-reagent grade chemicals from Kelong, Chengdu, China.

* Corresponding author at: College of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, China.
E-mail address: quanhp2005@swpu.edu.cn (H. Quan).

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Nomenclature

PPD	pour point depressant
FI	flow improver
TsOH	para-toluenesulfonic acid
MB	methylbenzene
C_i	the mass composition
A_i	the peak area
f_i	the weight correction factor of component
ν_u	the viscosity of untreated oil samples
ν_t	the viscosity of treated oil samples
W	the viscosity reduction rate
PE	pentaerythritol
PA	phthalic anhydride
C14	tetradecanol
C16	hexadecanol
C18	octadecanol
d	interplanar spacing
θ	incident line
λ	wavelength
n	reflection series

2.2. Elemental characterization

2.2.1. Crude oil characteristic analysis

The physical properties were analyzed and the result was listed in Table 1.The asphaltene, resin and wax were isolated from oil samples by the same way in the literature [25].

2.2.2. The carbon chain distribution of saturated hydrocarbon analysis

The saturated hydrocarbon was isolated from oil samples, dissolved in n-heptane and analyzed by gas chromatography-mass spectrometry (GC–MS, 7890A-5975C). Testing conditions: the temperature range from 40 to 100 °C at a heating rate of 5 °C/min, from 100 to 190 °C at a heating rate of 3 °C/min and from 190 to 300 °C at a heating rate of 2 °C/min. The injection volume is 10 μL/min.

We can quantify the relative mass percentage by normalization method:

$$C_i = \frac{A_i f_i}{\sum A_i f_i} \times 100\% \quad (1)$$

where C_i, A_i, f_i respectively indicates the mass composition, the peak area and weight correction factor of component. The f_i are very close 1 and approximate 1, so f_i defaults to 1.

The carbon number distribution of n-paraffin of crude oil was analyzed by gas chromatography-mass spectrometry and the partly result was given in Fig. 1. The proportion of tetradecane, hexadecane, octodecane in saturated hydrocarbon of crude oil is 1:1.40:8.29 after Calculation.

2.3. Synthesis of flow improver

High alcohols ($CH_3(CH_2)_nOH$, n = 13, 15, 17) and pentaerythritol were added in a round- bottomed flask which the para-toluenesulfonic acid as catalyst and methylbenzene as solvent to react two hours at 100 °C. Then, the temperature was decreased to 90 °C and phthalic anhydride was added to continue reacting 1 h. The whole reaction process was continuous stirring. After reaction over, poured out the liquid from the round-bottomed immediately and filtered by hot methylbenzene. Finally, evaporated the methylbenzene, drying and collecting the FI. The reaction is described in Fig. 2.

2.4. Evaluating test of viscosity

The apparent viscosity of crude oil samples were measured by rotational viscometer (NDJ-8S) with spindle No. 3 at a speed of 3 rpm. In the process of testing the viscosity of oil samples, recorded the first value when value displayed on instrument was basic stability, after every 5 min to record once. For four consecutive data, if the arithmetic mean of the last three data does not differ by more than 5% from the first data, the first data was the test result.

2.5. Thermogravimetric Analyzer (TGA)

The thermal analysis of flow improver was measured by Thermogravimetric Analyzer (TGA/SDTA851e), the test temperature was between 40 °C and 500 °C which raised temperature at a rate of 10 °C/min.

2.6. Infrared (IR) spectroscopy analysis

The chemical structure of the untreated and treated asphaltene, the untreated and treated resin were characterized respectively by means of infrared (IR) spectroscopy using WQF-520 FT-IR Spectrometer.

2.7. X-ray diffraction (XRD)

After adding the flow improver into the wax, the crystal lattice structure of the untreated and treated wax were studied by using X'Pert Pro X-ray diffraction (Cu·Ka, with a scanning rate of 1°/min and scanning range of 5° to 40°) from the Dutch PANalytical company.

2.8. Scanning electron microscope (SEM)

The asphaltene and resin were dissolved respectively in carbon tetrachloride and heated at 50 °C for 1 h. Then, some samples kept heating at 50 °C for 1 h, others were added FIs and also heated at 50 °C for 1 h, the untreated and treated samples was prepared after evaporating solvent. The configuration of surface and agglomerate structure of the untreated and treated samples were observed by scanning electron microscope (SEM, ZEISS EV0 MA15) at room temperature.

3. Result and discussion

3.1. The effect of flow improver

The FIs were synthesized in difference molar ratios of pentaerythritol, phthalic anhydride, octadecanol. The heating process ensures stirring frequently. The viscosity of untreated oil samples (ν_u) was test under 50 °C after oil samples had been placed at 50 °C for 2 h. The oil samples had been placed at 50 °C for 1 h before the FIs were added in a

Table 1
The Physical characteristics of the crude oil.

Crude oil	Viscosity (mPa·s,50 °C)	Pour point (°C)	Asphaltene (%)	Resin (%)	Saturated HC (%)	Aromatic HC (%)
Xinjiang	33430	28	0.81	7.19	36.53	55.47