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Original Paper

Synergistic effect of modified ethylene-vinyl acetate and asphaltenes on improving the flow properties of model oil

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ABSTRACT

The effect of alcoholic polyethylene-vinyl acetate (EVA) product ethylene-vinyl alcohol copolymer (EVAL) on the low-temperature flow properties of model oil containing asphaltene (ASP) was investigated. The change of wax crystal microscopic morphology of model oil before and after modification were examined, and the influence of asphaltene mass fraction on the rheological improvement effect of EVAL was analyzed. The composite system of EVAL and asphaltene significantly reduced the pour point, gel point, apparent viscosity, storage modulus and loss modulus of waxy oil at low temperatures. When the EVAL concentration is 400 ppm and the asphaltene mass fraction is 0.5 wt%, the synergistic effect of the two is optimal, which can reduce the pour point by 17 °C and the modulus value by more than 98%. The introduction of EVAL strengthens the interaction between asphaltenes and wax crystals, forming EVAL-ASP aggregates, which promote the adsorption of wax crystals on asphaltenes to form composite particles, and the polar groups prevent the aggregation of wax crystals and reduce the size of wax crystals, thus greatly improving the fluidity of waxy oils.
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1. Introduction

The wax in crude oil mainly refers to C_{16} to C_{40} *n*-alkanes (Aiyejina et al., 2011; Alcazar-Vara and Buenrostro-Gonzalez, 2011). When the temperature is lower than the wax apparent temperature (WAT), the wax molecules in waxy crude oil start to crystallize and precipitate due to supersaturation, and the precipitated wax crystals are needle-like or flaky, which can easily overlap each other to form a network structure (Mahmoud et al., 2006; Yao et al., 2016; Yi and Zhang, 2011). Therefore, the high pour point, poor flowability and complex rheological behavior make it difficult to transport waxy oil in the pipeline (Xie et al., 2023).

Asphaltenes are components of crude oil that are insoluble in *n*-heptane, but soluble in benzene or toluene (Garcia et al., 2000; Tinsley and Prud'homme, 2010). From the definition of asphaltenes, it is clear that asphaltenes are mixtures, containing a variety of functional groups (Rudrake et al., 2009) and multiple intermolecular interactions (Alemi et al., 2021; Oh et al., 2004). For this reason, it is quite difficult to study the behavior of asphaltene molecules. In recent years, the influence of asphaltene on the rheology of wax-containing oils has been a hot spot in the field of oil transportation (Huang et al., 2022; Moud, 2022; Sun et al., 2022; Zhang et al., 2021). The main content of the research is the effect of asphaltene concentration and polarity on the rheological properties (such as WAT (Yang et al., 2021), gelling temperature (Lei et al., 2014), yield stress (Li et al., 2018; Yao et al., 2018b), etc.) of waxy oil and its mechanism. Asphaltenes, as natural PPD, can modify the crystallization habit of waxes by acting as nucleation sites for wax crystals. Therefore, an in-depth understanding of the influence of wax and asphaltene content and chemical composition on the gelling and waxing characteristics and their mechanisms is important for the study of the gelling mechanism, modification mechanism and safe transportation of waxy oils. Because the components in crude oil are complex, the current international research on each component of flowability mainly utilized the technical line of research for model oil (You et al., 2019; Zhao et al., 2014).

Studies on the synergistic improvement of rheological properties of waxy model oils by asphaltene and polymeric PPDs are also emerging. Jiang et al. (2014) discovered that low concentrations of

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Abbreviations

EVA	Polyethylene-vinyl acetate
EVAL	Ethylene-vinyl alcohol copolymer
PPD	Pour point depressant
WAT	Wax apparent temperature
ASP	Asphaltene
MO	Model oil

asphaltene molecules can be fully dissolved in the oil, and during the cooling process, the dispersed asphaltenes can adsorb on the wax crystals like surfactants, preventing the wax crystals from increasing in size and thus improving the fluidity of the oil; while when the concentration increases, the interactions between asphaltene molecules intensify, causing the asphaltenes to aggregate and form large asphaltene aggregates, and these aggregates, together with the dense and regular wax crystals, increase the yield stress. Zhang et al. (2020) found that the introduction of the aromatic pendant in comb PPD strengthened the interaction between asphaltene and PPD and promoted the adsorption of PPD on asphaltene to form composite particles, which greatly improved the fluidity of waxy oil.

Polyethylene-vinyl acetate (EVA), as one of the widely used PPDs, the study of the interaction between EVA and asphaltene has also become the focus of attention of many scholars (Li et al., 2020; Xia et al., 2023; Yao et al., 2020). Yao et al. (2018c) found that poly(octadecyl acrylate) (POA) added with asphaltenes significantly reduced the pour point, gelling point, G', G'', and apparent viscosity of crude oil. In a follow-up study (Yao et al., 2017, 2018a, 2018b), it was systematically demonstrated that the addition of EVA improved the dispersion stability of asphaltenes in liquid paraffin. The composite particles favored the formation of large, dense, spherical wax flocs that released more liquid oil. The research done on how asphaltene affects the gelling properties of oil containing wax has primarily focused on the macroscopic rheological properties and mesoscopic wax crystal morphology. Understanding the wax precipitation properties of waxy oils is crucial for grasping the crystallization and movement of wax molecules within these oils, as well as for more precise calculations of the concentration gradient of saturated wax molecules. Both gelling properties and yield properties are measures of structural properties. They are closely related to the nature of the initial condensed oil layer during wax deposition and help to deepen the understanding of sediment exfoliation.

However, research on the effect of asphaltenes on the gelling and wax precipitation properties of waxy oils has not reached a consistent conclusion. Tinsley et al. (2009) found that at low asphaltene concentrations and high wax concentrations, there was no significant impact on the yield stress of the wax gels. However, at higher asphaltene concentrations, the presence of asphaltene notably disrupted the microstructure of the wax, leading to a significant reduction in the yield stress. It has also been found that asphaltenes form complex asphalt-paraffin solid aggregates and that the flocculation of asphaltenes reduces the effectiveness of wax inhibitors (García and Carbognani, 2001). The influence of low asphaltene concentrations on wax crystal precipitation is controversial, and these studies do not provide a systematic explanation of the mechanism of asphaltene influence on the gelling properties of waxy oil.

The alcoholic EVA product (EVAL) previously studied by our group has a good effect on crude oil fluidity (Liu et al., 2021), EVAL can further reduce the pour point of Daqing crude oil compared with EVA. At the optimal dosage of 1000 ppm, EVA can reduce the pour point by 6 °C, while EVAL can reduce the pour point by 10 °C. It also inhibits the low temperature viscosity, yield value and gel point temperature, which are improved to a certain extent compared with the EVA pour point depressants. The investigation of its action pattern in the model oil system has become the focus of interest, and the interaction between EVAL and asphaltene needs to be explored. In this research, the effect of EVAL and asphaltene synergy on the flow properties of waxy model oil was investigated. The change of wax crystal microscopic morphology of model oils before and after modification were examined, and the influence of asphaltene mass fraction on the rheological improvement effect of EVAL PPD was analyzed. And the mechanism of the synergistic effect of the two is speculated from the microscopic images of wax crystal molecules.

2. Materials and methods

2.1. Materials

Methanol (AR), toluene (AR), sodium hydroxide (NaOH), dodecane and *n*-heptane were all obtained from Aladdin Reagent Co., Ltd. (Shanghai). The vinyl acetate content of the EVA which was obtained from Mitsui Chemicals (Japan) was 26 wt%. EVAL is synthesized by reacting ethylene-vinyl acetate with methanol in the presence of sodium hydroxide as a catalyst (Liu et al., 2021). Most of the ester groups of EVA are replaced by hydroxyl groups. Paraffin and 0# diesel oil utilized within the analysis were obtained from Daqing Oilfield, Heilongjiang, China. The crude oil used for asphaltene extraction is taken from Tahe crude oil, Xinjiang, China. The physical properties of the Tahe crude oil are presented in Table 1.

2.2. Sample preparation

Model oil (MO) containing 20 wt% wax was prepared by dissolving paraffin in 0# diesel oil and then stirring at 60 °C for 2 h (Jing et al., 2017). The synthesis process of EVAL is referred to previous studies (Liu et al., 2021). The asphaltene extraction process is as follows: Tahe crude oil was added to the flask and *n*-heptane was poured into the flask, which was gently shaken and put into a heating jacket for refluxing. Next, the filter paper with insoluble material was placed in an extractor and extracted with toluene for about 1 h until the solution in the extractor appeared colorless. The asphaltene solution was then concentrated by a rotary evaporator for at least a minimum amount and then dried in a vacuum oven, and the solid material obtained was asphaltene (Ashoorian et al., 2021; Li et al., 2020; Xue et al., 2019). To avoid the aging of asphaltenes due to oxygen or light, the asphaltenes are stored in a dark environment, sealed from light (Liu et al., 2020). Different mass fractions of asphaltenes were added to the simulated oil based on the calculated mass fractions to perform the subsequent experimental measurements, the experimental procedure is shown schematically in Fig. 1 and care should also be taken to avoid disturbance of the properties of the simulated oil by repeated heating.

2.3. Relevant characterization of asphaltenes

The chemical structures of asphaltenes were confirmed utilizing Fourier transform infrared (FTIR) spectroscopy using a Bruker TENSOR II infrared spectrometer. XRD for asphaltenes was obtained

Table 1
Physical properties of Tahe crude oil.

Resins, wt%	Asphaltenes, wt%	Wax, wt%	Density
22.3	19.1	0.5	0.910

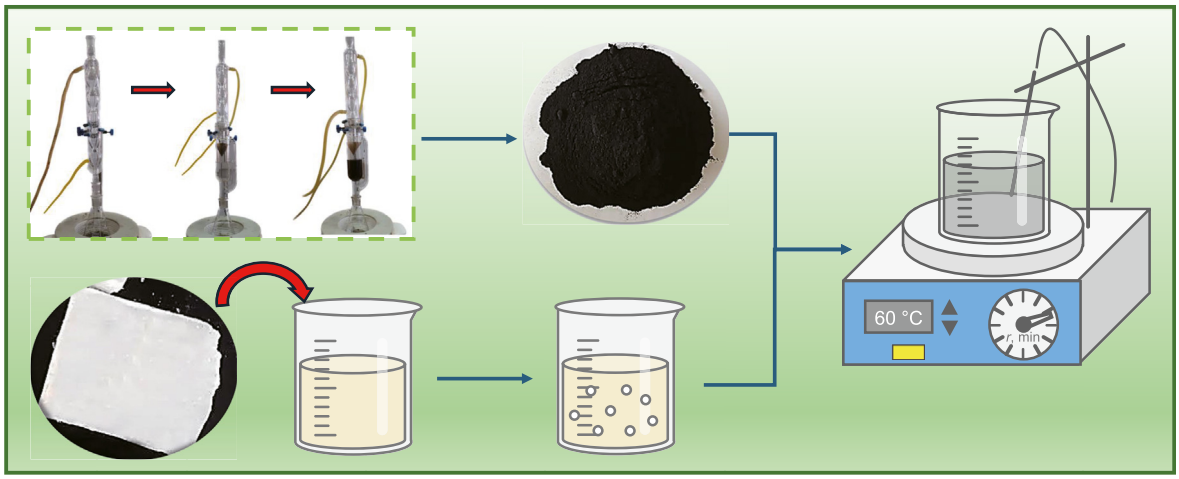


Fig. 1. Schematic diagram of the experimental process.

using a SmartLab SE XRD diffractometer (Rigaku Corporation Co. Ltd., Japan) (40 kV, 30 mA) with Cu Kα, and the sample scanned at 2θ from 5° to 80° at a rate of 10°/min. To determine the particle size distribution of the asphaltenes, the ASP was ultrasonically dispersed and heated until they are fully dissolved in dodecane. A nanoparticle size analyzer (NANO ZS90, Malvern, Britain) was used and the average results were calculated. The morphology of asphaltenes was assessed with field emission scanning electron microscopy (Quanta 200 FEG, FEI, USA) was used.

2.4. Pour point test

The model oil was preheated for 1 h at 60 °C in a water bath with heating conditions to eliminate its thermal history. The pour point of oil samples was determined using the standard ASTM D97-17a method.

2.5. DSC test

The DSC curves of the oil samples were measured by a Differential Scanning Calorimeter from TA, USA. The samples were cooled from 80 to −20 °C at a constant cooling rate (5 °C/min).

2.6. Verification of viscosity-temperature change curve

The oil sample was placed into the DHR-1 Advanced Hybrid Rheometer (TA Instruments, USA), thermostated at 60 °C for 20 min, and sheared at a fixed shear rate (20 s^{-1}), while the temperature was decreased from 60 to 10 °C at a cooling rate of 0.5 °C/min, and the apparent viscosity was measured with temperature reduction.

2.7. Gel characteristics of undoped and doped oil

The viscoelasticity laboratory in oscillatory mode is an effective way to study the process of sol-gel transition of oil samples under static cooling conditions. The preheated oil samples were put into a rheometer and kept at a constant temperature of 60 °C for 1 h, followed by oscillation at a cooling rate of 0.5 °C/min to 15 °C, and the strain of the rheometer was set to 0.0005 and the oscillation frequency was 1 Hz, and the storage modulus G' and loss modulus G'' were recorded during the cooling process.

2.8. Polarized optical microscopy

A polarized optical microscope (ZEISS AXIO, Germany) was used to observe the wax crystal morphology of the oil sample before and after the addition of nanocomposite PPD at a certain temperature. The oil samples were heat-treated at 60 °C for 20 min, then loaded onto the microscope hot stage and cooled down from 60 to 15 °C at a cooling rate of 0.5 °C/min, and polarized micrographs of the oil samples at 15 °C were taken.

3. Results and discussion

3.1. Characterization of the asphaltenes

It is clear in Fig. 2(a) that the spectrum of ASP shows characteristic absorption bands at 1400 cm^{-1}, which can be attributed to the shear bending vibration of CH_2. The peaks in 1144, 1645 and 2920 cm^{-1} represent the stretching vibration of C—O, C=O and C—H, respectively (Jaberi et al., 2020). The presence of chain alkanes in the asphaltene structure can be identified. Moreover, peaks in the wavenumbers of 862 cm^{-1} are assigned to the C—H in-plane bending vibrations in aromatic rings, and the peaks in 1607 cm^{-1} are related to the stretching vibration peak of C=C in the benzene ring. Such a spectrum displayed absorption bands at 3131 and 3421 cm^{-1} can be attributed to the stretching vibration of amine and carboxyl groups and it indicates that there is hydrogen bonding between asphaltenes. It is concluded that the asphaltenes are polar molecules with aromatic rings, heterocyclic aromatic hydrocarbons, long-chain alkanes and hydrogen bonds.

Fig. 2(b) showed the X-ray diffraction pattern of the asphaltenes. The two intense peaks at 19° and 26° were markedly observed. The characteristic diffraction peak at 19° is caused by alkyl side chains in asphaltene molecules and responds to the degree of stacking of alkyl side chains. the diffraction peak near 26° is derived from the diffraction of thick-ringed aromatic layers (Christopher et al., 1996), which characterize the graphitized aromatic carbon diffraction peak.

The particle size distribution of the asphaltenes was shown in Fig. 2(c). The distribution in the figure confirms that the asphaltene has a narrow particle size distribution area in the oil phase with an average particle size value of 1.29 μm, reaching a good degree of dispersion in the oil phase (Yao et al., 2020).

Asphaltenes are complex mixtures in composition, resulting in poor homogeneity of surface morphology and no fixed

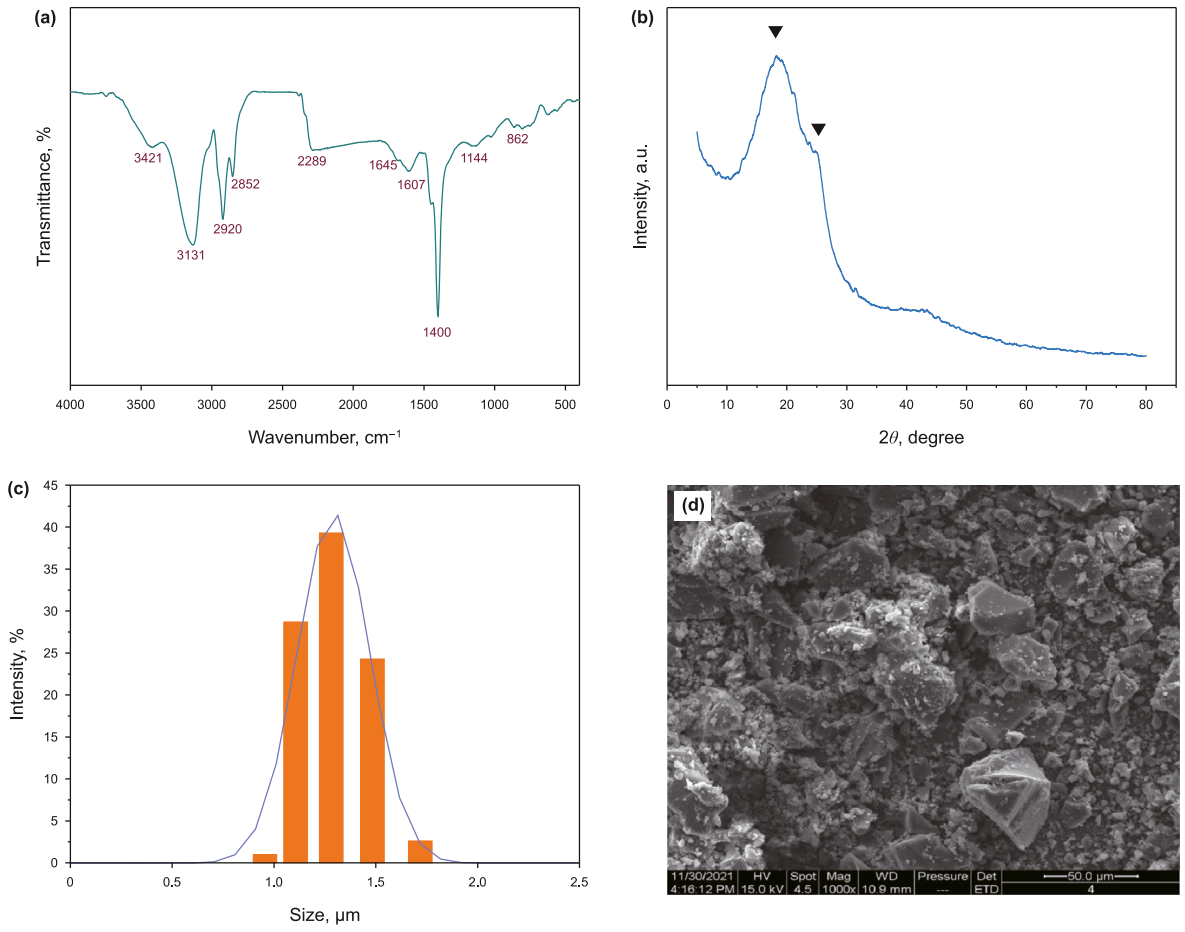


Fig. 2. Asphaltene structure characterization results: **(a)** FTIR spectra; **(b)** X-ray diffraction pattern; **(c)** particle size distribution; **(d)** scanning electron microscope image.

morphology. Fig. 2(d) shows the scanning electron micrograph of ASP. From the surface morphology, it can be observed that the asphaltene of Tahe is formed by the accumulation of non-uniform lamellar particles with dense accumulation, and it is easy to accumulate into a “crystal core” (Quan et al., 2018). This morphology also directly affects the subsequent interaction with wax crystals.

3.2. Effect of the asphaltene on the properties of doped model oils

3.2.1. Pour point depression effect

The test results of the pour point are presented in Fig. 3. The pour point of the blank model oil sample was known to be 32 °C, and the mass fraction of asphaltene added was 0.5 wt%. In the blank model oil, there was no significant change in the pour point when EVA and EVAL were added separately, which indicates that the selected EVA and modified EVA did not have any effect on the pour point of this model oil system. The reason for this phenomenon may be the mismatch between the alkyl long chains of EVA and the carbon number distribution of the waxes in the model oil (Alves et al., 2023; Da Silva et al., 2004). However, a decrease in the pour point was observed after the addition of asphaltene. The initial pour point of the blank model oil is 28 °C after the addition of asphaltene and the concentration of EVA additive at 400 ppm reduced the pour point to 24 °C, which indicates that asphaltene can contribute to the reduction of the pour point of the oil sample. Further, the addition of EVAL and asphaltene increased the reduction of the pour point of model oil, which could reduce the pour point to 15 °C under the optimal addition rate (400 ppm). Compared with the EVA + ASP system, a further reduction of 9 °C was achieved. The results indicate that the composite system composed of EVAL and asphaltene can synergistically reduce the pour point.

3.2.2. Crystallization exothermic curve of model oils

Fig. 4 showed the DSC curves of the model oils under different conditions. The WAT of the model oils without additives was 32.8 °C, and the addition of 0.5 wt% asphaltene alone could reduce theWAT from 32.8 to 29.4 °C. Due to the large number of alkyl side chains in the asphaltene, the asphaltene could co-crystallize with the wax molecules in the process of cooling down, which suppressed the wax crystals' precipitation, and thus lowered the WAT. With the addition of 400 ppm EVAL, the WAT was further reduced to 26.8 °C. The strong polar groups in the structure of EVAL increase the interfacial tension between the wax crystals and the oil phase, raise the nucleation barriers for the wax molecules to crystallize, and the wax molecules to crystallize in the oil phase. and increase the nucleation barrier of the wax molecules, which makes it difficult for the wax molecules to be precipitated out, thus further reducing the temperature at which the wax crystals start to precipitate.

3.2.3. Viscosity-temperature curve

The change of undoped/doped model oil viscosity with temperature during the cooling process is demonstrated in Fig. 5. In general, the rheological behavior of the three waxy model oil systems is consistent. When the temperature approaches the critical

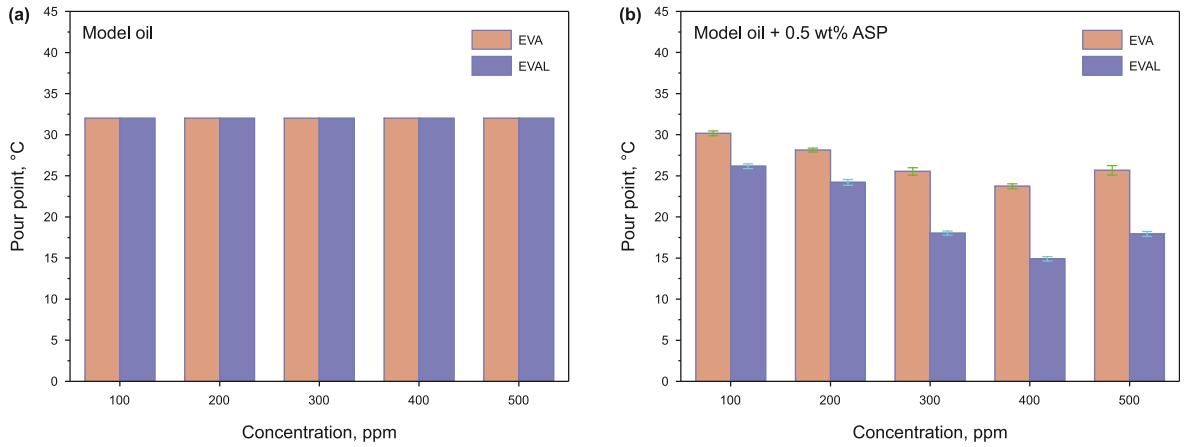


Fig. 3. Pour point depression results of EVA and EVAL in different systems: **(a)** model oil; **(b)** model oil+0.5 wt% ASP.

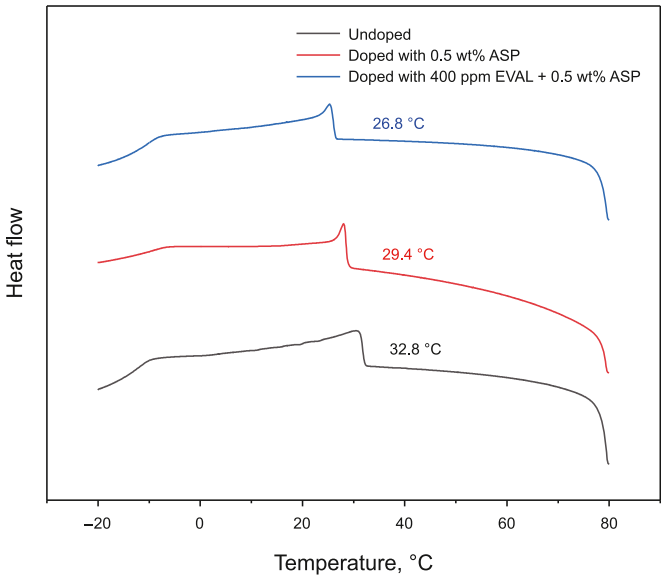


Fig. 4. DSC curves of modeled oils under different conditions.

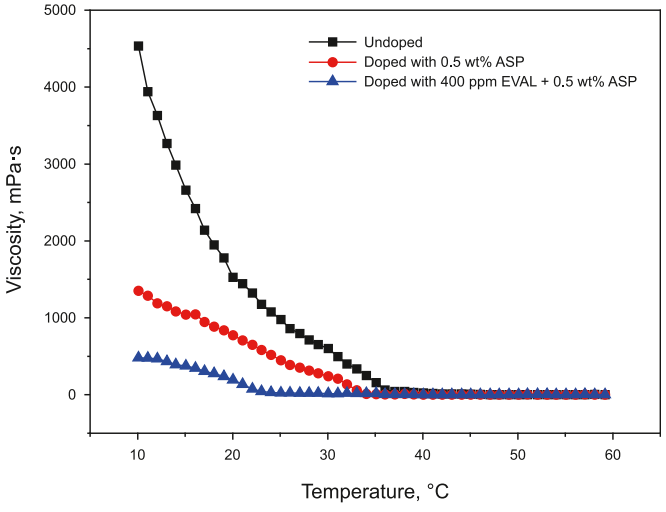


Fig. 5. Viscosity-temperature change curve of undoped/doped model oil.

temperature, the system assumes a Newtonian fluid state, and the apparent viscosity is almost constant at this time. As the temperature decreases further, the apparent viscosity starts to increase sharply and the rheological behavior changes to a non-Newtonian state (Alcazar-Vara et al., 2012). The results show that the viscosity gradually increases with decreasing temperature in the non-Newtonian region for both asphaltene-containing and non-asphaltene-free waxy model systems.

As shown in Fig. 5, the apparent viscosity of the oil samples decreased significantly after the addition of asphaltene. The apparent viscosity of the blank oil sample was 4534.83 mPa s at 10 °C, which was reduced to 1351.98 mPa s with the addition of 0.5 wt% ASP. After loading 0.5 wt% ASP and 400 ppm EVAL, the apparent viscosity at 10 °C was further reduced to 479.81 mPa s. The corresponding average viscosity reduction rate of the unloaded simulated oil was 89.4%, an improvement of 19.2% compared to the addition of asphaltene alone (70.2%). The critical temperatures corresponding to the sharp increase in viscosity of the undoped oil sample, doped with asphaltene and doped with asphaltene with EVAL model oil during cooling were 37.1, 34.1 and 24.0 °C, respectively. The above results show that the addition of asphaltene can improve the viscosity-temperature characteristics of waxy model oils, and EVAL and ASP can act synergistically to further reduce the low-temperature viscosity and critical temperature.

3.2.4. Gel characteristics results

Fig. 6 shows the whole viscoelastic change process of model oil with temperature decrease for different systems. When the temperature is in the higher range, the values of both the storage modulus G' and loss modulus G'' are small, indicating that the elastic component of the model oil is less at this time. The above results show that the paraffin in the model oil hardly precipitates at high temperatures, and therefore the flow properties of the model oil do not change as a consequence.

As the temperature decreases, there is a sudden rise stage of both G' and G'', indicating that the oil sample has been transformed from Newtonian fluid to non-Newtonian fluid, and when the values of G' and G'' are equal, the oil sample forms a gel structure, and the corresponding temperature at this time is called the gel point temperature. With a further decrease in temperature, the concentration of wax crystals precipitated in the waxy model oil gradually increases, the gel structure of the oil sample system becomes more and more complex, and its non-Newtonian fluid nature becomes stronger and stronger. When the concentration of wax crystals increases to a certain degree, the flocculated wax crystals develop

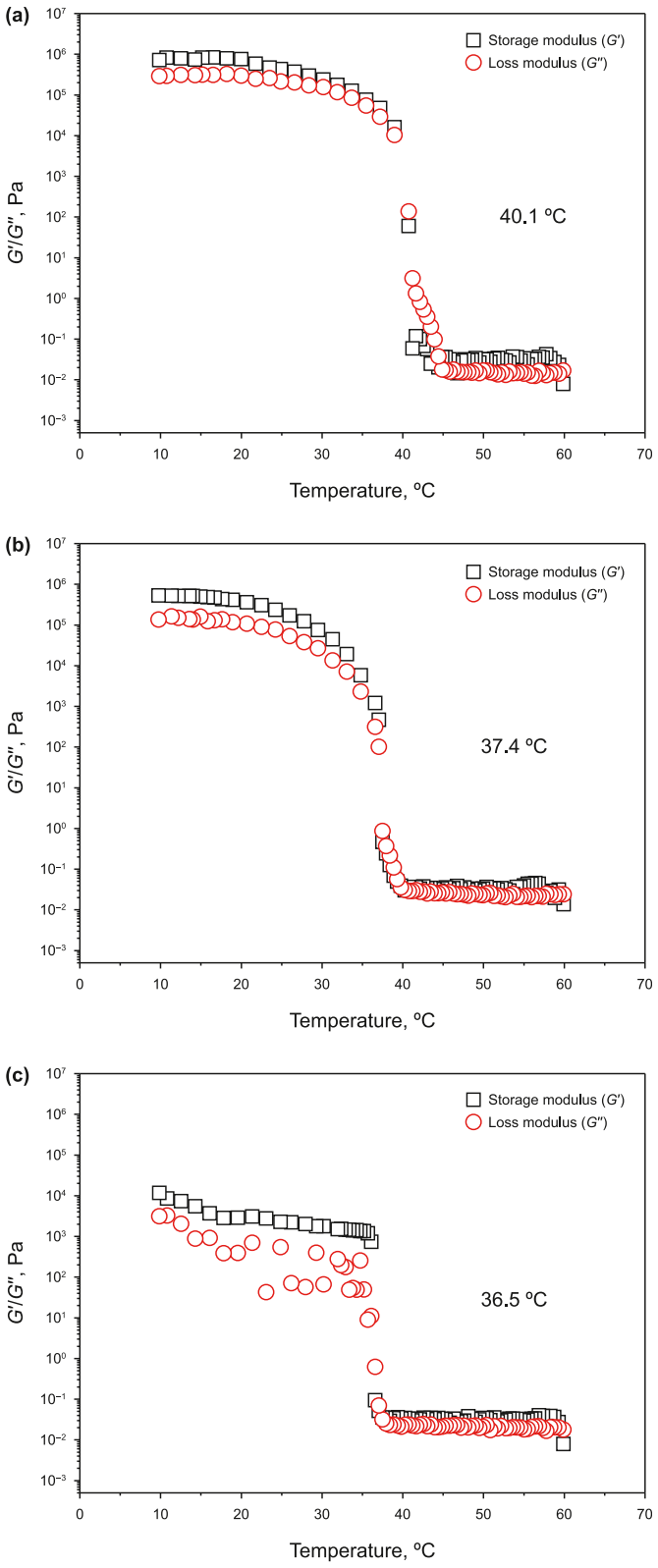


Fig. 6. Viscoelasticity curves for different systems of waxy model oils: **(a)** Undoped; **(b)** doped with 0.5 wt% ASP; **(c)** doped with 0.5 wt% ASP+400 ppm EVAL.

into a dense three-dimensional mesh structure, and the liquid oil is embedded between the wax crystals, thus losing its fluidity (Yao et al., 2020).

As can be seen in Table 2, The addition of asphaltenes decreased the gel point by 2.7 °C and lowered the G' and G'' values, indicating that asphaltenes can inhibit the formation of gel structure and weaken the strength of the gel structure. The gel point of the oil was lowered. With the addition of EVAL within the composite system, the gel point of the oil sample was further reduced to 36.5 °C, and both G' and G'' values at 10 °C underwent a significant reduction, by 98.58% and 98.94%, respectively, compared to the blank oil sample, and by 97.8% and 97.65% compared to the asphaltene system alone, indicating that the synergistic effect of EVAL and asphaltene can greatly reduce the strength of the gel structure, which means that the formed gel structure is very fragile and the flowability can be well improved.

3.2.5. POM analysis

The microscopic morphology of wax crystals of the initial and doped model oil is shown in Fig. 7. It can be seen that the wax crystals of the blank model oil (Fig. 7(a)) are larger, while the addition of EVA (Fig. 7(b)) is dominated by a large number of fine needle-like wax crystals with a high number of particles, which can easily lap each other to form a network structure. After doping with EVAL (Fig. 7(c)) the degree of aggregation of wax crystals increased significantly, the number of wax crystals increased and the size became smaller, but the shape did not change and was still needle-like. This also echoes the pour point data that the addition of EVA and EVAL alone did not improve the low-temperature fluidity of the model oil. Although the pour point data did not change significantly, the number of wax crystals precipitated showed that EVAL made more wax crystals precipitate earlier due to its own stronger polarity.

With the loading of ASP, the initial model oil starts to form wax crystal aggregates with asphaltene agglomerates as the growth centers (Moud, 2022; Zhang et al., 2020), as exhibited in Fig. 7(d). While EVA can be adsorbed on asphaltene to form EVA/asphaltic composite particles as shown in Fig. 7(e), which can be used as a non-homogeneous template for the crystalline precipitation of wax molecules, forming flower cluster-like, larger size and denser structured wax crystal aggregates compared with Fig. 7(b). Comparing Fig. 7(c) and (f), in the presence of both ASP and EVAL within the waxy model oil system, the microscopic morphology of the wax crystals is significantly improved and the needle-like structure disappears. Since EVAL is strongly polarized, when asphaltene is also present, the polar groups can adsorb on asphaltene (Xia et al., 2023) and form new aggregates with the wax crystals, reducing the mutual lap between the wax crystal particles, and the gap between the wax crystals and the wax crystals increases. The strength of the wax crystal spatial network structure is weakened, which explains the decrease in gel temperature and the values of G' and G''. Analysis of the degree of molecular association shows that the association structure between the strongly polar EVAL and the strongly polar asphaltene is stable, and the modification of the wax crystal morphology is excellent.

3.3. Effect of the asphaltene content on the characteristics of model oils

3.3.1. Pour point test results

The pour point is the most intuitive parameter reflecting the

Table 2
Gel characteristics parameters of waxy model oils in different systems.

Model oil system	Gel point, °C	G' at 10 °C, Pa	G'' at 10 °C, Pa
Undoped	40.1	825372	296416
+0.5 wt% ASP	37.4	535942	135775
+0.5 wt% ASP+400 ppm EVAL	36.5	11756	3148

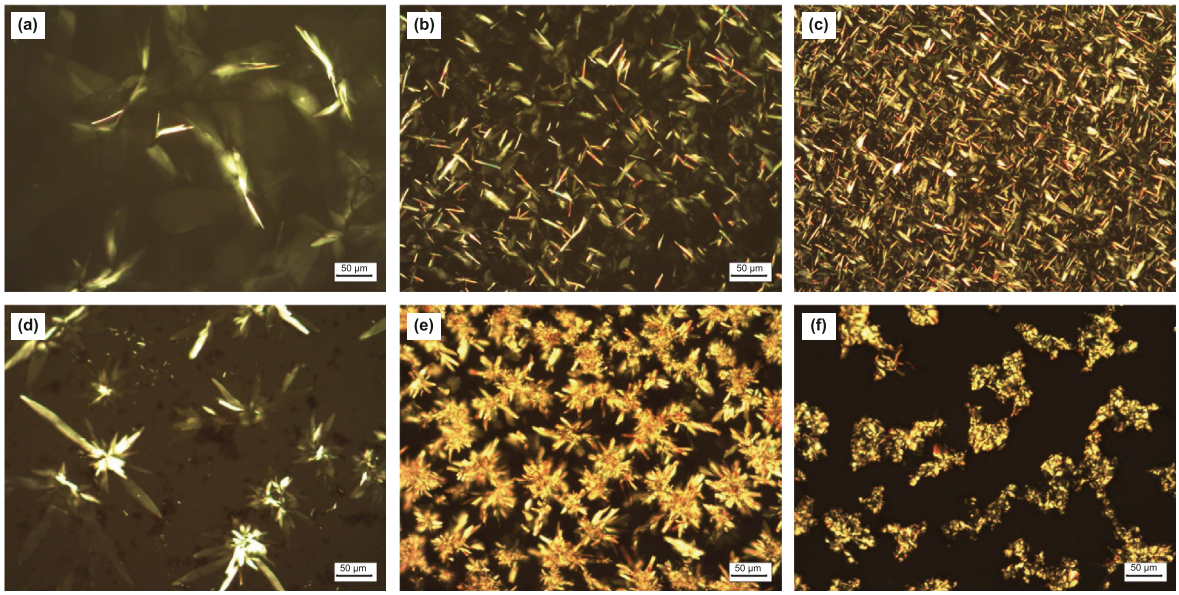


Fig. 7. Polarized microscopic analysis of the samples: **(a)** MO; **(b)** MO + EVA; **(c)** MO + EVAL; **(d)** MO + ASP; **(e)** MO + EVA + ASP; **(f)** MO + EVAL + ASP.

low-temperature flow properties of the oil sample. Fig. 8 illustrates the effect of the system with different concentrations of EVAL on the pour point of the waxy model oil under different asphaltene content conditions. The most obvious observation from the graph is that asphaltene, as a natural PPD, causes a decrease in the pour point with all four mass fractions of ASP when added individually. With the incorporation of EVAL in the system, the pour point decreases further. With the increase of EVAL concentration, the pour point showed a trend of decreasing and then increasing, and the best effect was achieved at 400 ppm. On the other hand, the influence of asphaltene content on the pour point is also significant, and the best effect of pour point suppression is achieved when the asphaltene content is 0.5 wt%, after which the pour point shows a tendency to increase instead when the ASP content is increased again. Combined with the information of the 3D histogram, when the asphaltene content in waxy model oil is 0.5 wt% and EVAL concentration is 400 ppm, the synergistic effect of the two is the best and the pour point is best inhibited.

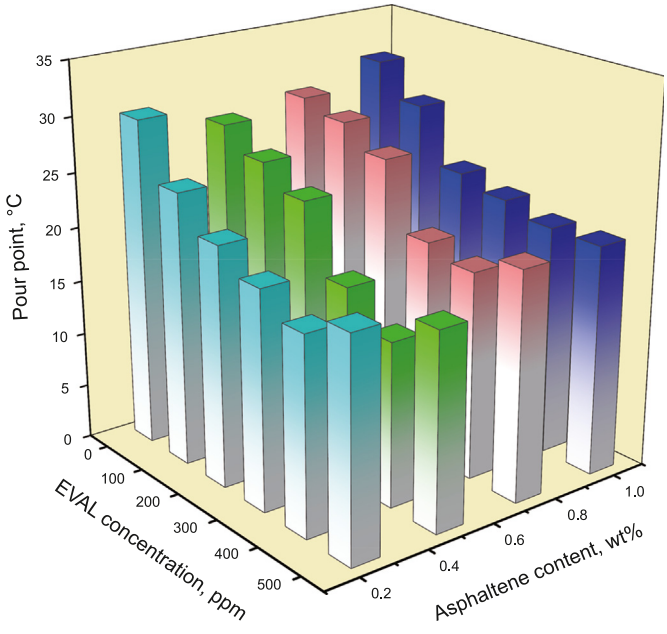


Fig. 8. Effect of the asphaltene content on the pour point of the model oils doped with different concentrations EVAL.

3.3.2. Analysis of viscosity changes

The curves of the apparent viscosity of waxy model oil with time for a fixed shear rate of 20 s^{-1} and EVAL dosing rate of 400 ppm with different mass fractions of asphaltene are presented in Fig. 9. The four curves showed the same trend when the temperature was lower than the critical temperature, the viscosity started to rise sharply. The apparent viscosity values were 666.656, 479.81, 798.611, and 1032.985 mPa s for the four systems at a temperature of 10 °C and ASP contents of 0.25, 0.5, 0.75, and 1 wt%, respectively, and the corresponding critical temperatures were 27.08, 24.04, 34.12, and 35.13 °C. The viscosity and temperature curves were consistent with the pour point test results, which indicated that the

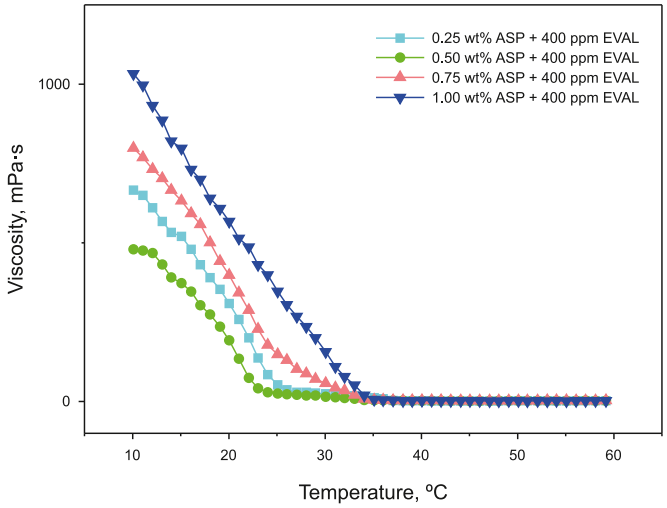


Fig. 9. Impact of asphaltene mass fraction on the viscosity of waxy model oil.

synergistic effect of asphaltene and EVAL was influenced by the asphaltene content, and the apparent viscosity showed a trend of decreasing and then rising with the increase of asphaltene content. An increase in asphaltene concentration may lead to aggregation between ASPs, increasing the viscosity of the sample. And the optimal viscosity reduction performance was reached at 0.5 wt% of asphaltene content.

3.3.3. Gel characteristics analysis

The viscoelastic curves of the model oil loaded with different mass fractions of asphaltene are shown in Fig. 10. The curves have approximately the same trend, and all of them reduce the gel point, storage modulus and loss modulus to some extent. In particular, the values of G' and G'' were both reduced by several orders of magnitude compared to the blank oil samples, indicating that the synergistic effect of EVAL and ASP on the gel structure was the most pronounced.

For the sake of comparison, the G' and G'' values of EVAL-doped waxy models with oil at 10 °C are summarized in Table 3 for different asphaltene contents. The best synergistic effect of EVAL and ASP was achieved when the asphaltene concentration was 0.5 wt%, which was also consistent with the results of the viscosity-temperature curve. The increase in asphaltene concentration made the system excessively polar, and the improvement effect became worse.

3.3.4. Wax crystal morphology study

From Fig. 7, it is clear that asphaltene in the model oil has the effect of changing the morphology and number of wax crystals. The effect of asphaltene concentration on the synergistic effect of EVAL and ASP is explained from the perspective of wax crystal morphology. As shown in Fig. 11, after the asphaltene concentration in the model oil increased, the size of wax crystal aggregates suspended in the model oil became larger and the mobility property became poorer at the same temperature. The reason for this phenomenon may be that ASP tends to aggregate into aggregates with large particle size and wide distribution due to the increase of asphaltene concentration (Enayat et al., 2020), which also leads to the increase of wax crystal volume in the EVAL-ASP system.

By observing Fig. 11(a)–(d), it is evident that the wax crystal morphology is highly responsive to variations in asphaltene concentration. Even slight adjustments in mass fraction can lead to significant alterations in microscopic morphology. Moreover, the introduction of EVAL causes the wax crystals in the system to tend to form more regular shaped, smaller and finer crystals. Suitable asphaltene concentration will better synergize with EVAL to

Table 3
Gel characteristics parameters of model oil with different ASP content in the presence of 400 ppm EVAL.

ASP content, wt%	Gel point, °C	G' at 10 °C, Pa	G'' at 10 °C, Pa
0.25	36.9	13265	3335
0.50	36.5	11756	3148
0.75	37.6	29731	10483
1.00	37.7	55618	21006

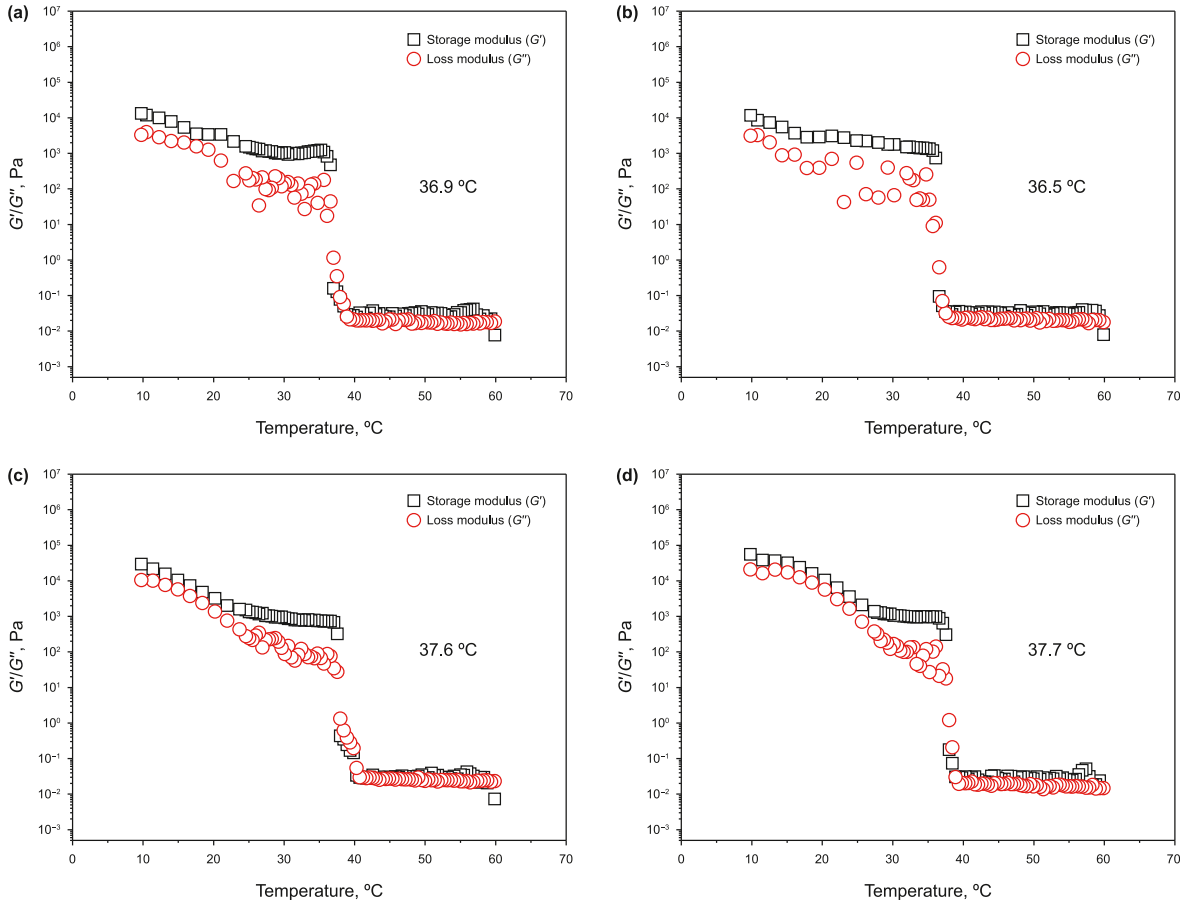


Fig. 10. Viscoelasticity development of the waxy model oil during the cooling process: doped with **(a)** 0.25 wt% ASP+400 ppm EVAL; **(b)** 0. 50 wt% ASP+400 ppm EVAL; **(c)** 0.75 wt% ASP+400 ppm EVAL; **(d)** 1.00 wt% ASP+400 ppm EVAL.

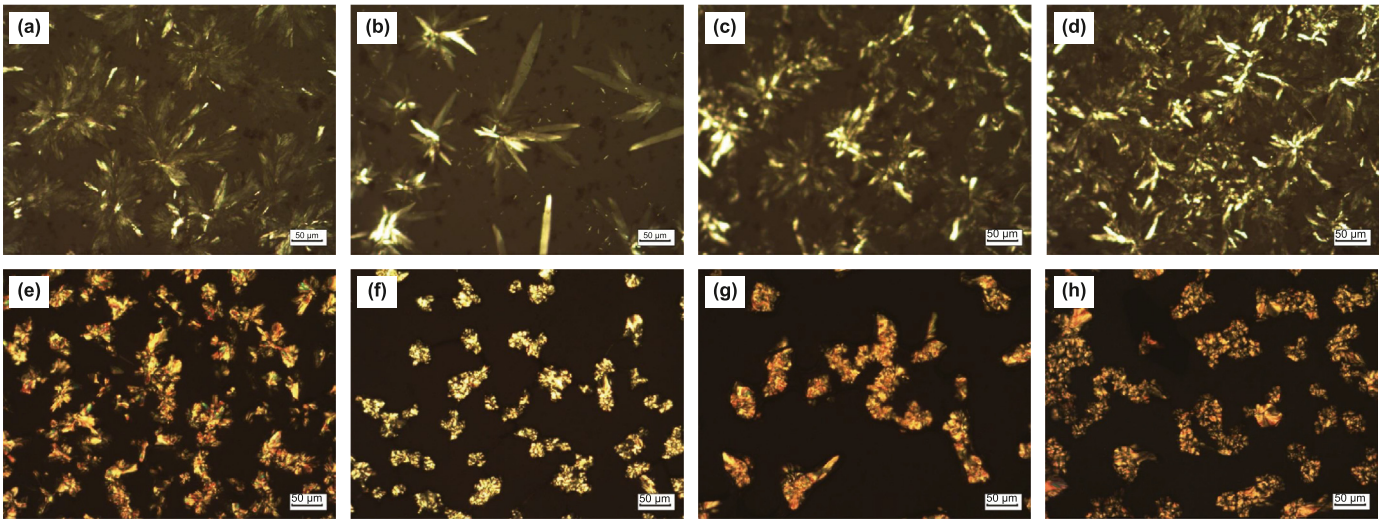


Fig. 11. Influence of the asphaltene content on the wax microstructure: **(a)** MO+0.25 wt% ASP; **(b)** MO+0. 50 wt% ASP; **(c)** MO+0.75 wt% ASP; **(d)** MO+1.00 wt% ASP; **(e)** MO+0.25 wt% ASP+400 ppm EVAL; **(f)** MO+0.50 wt% ASP+400 ppm EVAL; **(g)** MO+0.75 wt% ASP+400 ppm EVAL; **(h)** MO+1.00 wt% ASP+400 ppm EVAL.

improve the microscopic image of wax crystals and release more oil phase, which enables a deeper promotion of the low-temperature flow properties of the model oil system.

3.4. Mechanism

In Fig. 12, the possible mechanism for the synergistic improvement of the flow properties of waxy model oils by EVAL and asphaltene is presented. The introduction of EVAL strengthens the interaction between asphaltenes and wax crystals, forming EVAL-ASP aggregates, which promote the adsorption of wax crystals on asphaltenes to form composite particles, and the polar groups prevent the aggregation of wax crystals and reduce the size of wax crystals, thus greatly improving the fluidity of waxy oils. However, with the increasing asphaltene concentration, the agglomeration between ASPs will inhibit the improvement of wax crystal morphology, which is not conducive to the improvement of flow properties.

4. Conclusions

In this research, the effect of EVAL and asphaltene synergy on the flow properties of waxy model oil was investigated. The composite system of EVAL and asphaltene significantly reduced the pour point, gel point, and apparent viscosity, storage modulus and loss modulus of waxy oil at low temperatures. Compared with EVA, EVAL is more polar and has better interaction ability with asphaltene. When the EVAL concentration is 400 ppm and the asphaltene mass fraction is 0.5 wt%, the synergistic effect of the two is optimal, which can reduce the pour point by 17 °C and the modulus value by more than 98%. Moreover, the analysis of wax crystal micromorphology shows that the wax crystal particles increase the gap between wax and wax crystal by adsorbing in the new nucleation sites composed of EVAL and asphaltene, which significantly reduces the strength of the spatial network structure of the wax crystal, thus significantly improving the flow characteristics and low-temperature gelling structural properties. As the asphaltene content increases, the aggregation between ASPs decreases the improved efficiency, which leads to poor flow properties. This study further develops the theoretical system that polymer and asphaltene synergistically affect the flowability of waxy model oil and also provides an aid to explore the relationship study between asphaltenes and different polar compounds.

CRediT authorship contribution statement

Yang Liu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Zheng-Nan Sun:** Visualization, Methodology. **Guo-Lin Jing:** Supervision, Resources, Investigation. **Yi-Hai Yang:**

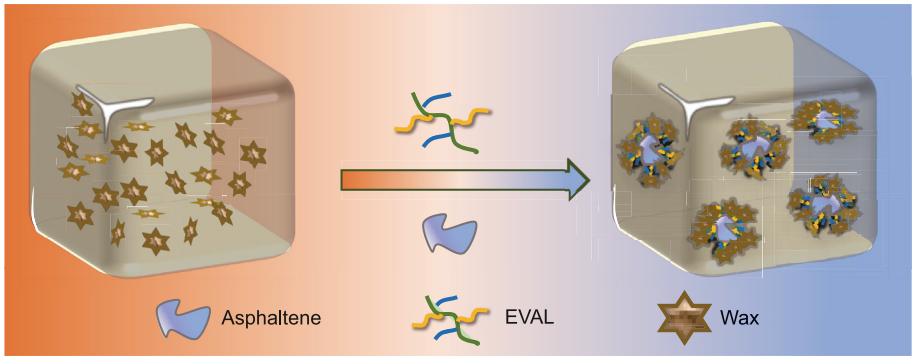


Fig. 12. Possible mechanism of EVAL and asphaltene synergistically improving the flow properties of waxy model oil.

Investigation, Formal analysis. **Hui Jiang:** Investigation, Formal analysis. **Xiao-Yan Liu:** Supervision, Funding acquisition.

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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