



## Original Paper

# Performance improvement of Ethylene–Vinyl Acetate Copolymer Pour Point Depressant (EVA PPD) by adding small dosages of Laurylamine (LA)

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## ABSTRACT

Laurylamine is widely considered to be an asphaltene flocculant, but its effect on the modification of crude oil by PPDs has been little studied. In this paper, the effect of LA dosage on the rheology improvement of EVA PPDs (100 ppm) on Qinghai waxy crude oil was investigated through rheological measurement, wax precipitating analysis, granularity test and resins/asphaltenes FTIR analysis. Compared with pure EVA, the compounding of LA and EVA obviously enhances the agglomeration degree and reduces the number of fine wax crystals, thus further enhancing the rheology of the oil samples, and the best performance is at the LA dosage of 200 ppm. At relatively small LA dosages, the LA facilitates the adsorption of EVA molecules on the asphaltene surfaces, which favors the becoming of EVA/asphaltenes composite particles; but at relatively high LA dosages, the LA makes the asphaltenes more aggregated and disturbs the EVA adsorption on the asphaltenes, which is adverse for the formation of EVA/asphaltenes compound particles. The compound particles can serve as wax precipitating templates and significantly influence its morphology, thus further improving the crude oil rheology. In consequence, the rheology improvement of EVA PPDs on Qinghai waxy crude oil first increases and then decreases with increasing the LA dosage. © 2022 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Waxy crude oil is one of the significant fossil fuels and is frequently found all around the world. When the temperature is below the wax appearance temperature (WAT) of waxy crude oil, paraffin wax precipitates as needlelike or lamellar wax crystals because of oversaturation (Moussa, 2001, 2002; Yang et al., 2014). With the oil temperature decreases, the amount of the precipitated wax crystals increases significantly, thus seriously deteriorating the fluidity of waxy crude oil. The aggravated fluidity makes the pipeline transmission storage and recovery of waxy crude oil more problematic (Aiyejina et al., 2011; Sarita et al., 2013; Yang et al., 2014). To ensure the safe recovery and pipelining of the oil, it is

normally heated to relatively high temperatures so as to maintain appropriate flowability. However, heating the oil is not only energy-consuming but has poor social and environmental benefits, which prompts researchers to explore more efficient ways to enhance the flowability of waxy crude oil.

At present, polymeric pour point depressants (PPDs) are often selected to modify the fluidity of waxy crude oil. Although the dosage of PPDs is low (dozens to hundreds  $\text{mg}\cdot\text{kg}^{-1}$ ), the PPDs could effectively improve the low-temperature flowability of waxy crude oil. The commonly used polymeric PPDs include polyethylene–vinyl acetate (EVA) series, polyacrylate series, maleic anhydride copolymers and nitrogen-containing polymers (Yang et al., 2016; Yao et al., 2018). The molecular structure of the PPDs generally covers two parts: non-polar long-chain alkanes ( $\text{C}_{16}\sim\text{C}_{22}$ ) which can interact with wax molecules and polar groups (including anhydride group, ester group and amide group) which can affect the dispersion state of wax crystals (Alves et al., 2019; André and Machado, 2001; Fang et al., 2012; Joonaki et al., 2020; Pedersen,

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2003; Yang et al., 2014, 2016, 2018; Yao et al., 2018; Zhang et al., 2014). As a mature industrial product, EVA has been widely used in oilfield and transmission pipelines as PPDs due to its good performance.

A lot of work has been carried out to discover the mechanisms and action laws of EVA PPDs (Jin et al., 2014; Machado and Lucas, 1999; Yang, 2009). The EVA molecules could not obviously decrease the quantity of wax precipitation at relatively low temperatures, but can dramatically modify the microstructure of wax crystals through the co-crystallization effect, thus greatly enhancing the rheological properties of waxy crude oil. The molecular structure of EVA is in direct relation to the performance of it. The VA content is a key factor of the performance of EVA, and the optimal performance is verified at the VA content around 28 wt %. To further enhance the performance of EVA, Ren et al., 2017, 2018 first modified the VA group by alkali-catalyzed alcoholysis reaction, and then grafted *n*-alkyl acrylates into the EVA molecules. They found that the modified EVA could significantly influence the process of wax crystallization and reduce the quantity of precipitated wax crystals of crude oil, enabling further enhancement of the rheological properties of waxy crude oil. The performance of EVA is also affected by the composition of oil samples, such as the wax content, the wax carbon number distribution and asphaltenes. With the increase of the content or the mean carbon number of the wax, the efficiency of EVA is often decreased (Machado and Lucas, 1999; Xie et al., 2020; Yang et al., 2017; Yang, 2009; Yang et al., 2018; Yang et al., 2018).

Asphaltene, which is normally composed by a polycyclic aromatic ring core as well as ortho- and iso-alkyl side chains, are the most polar component of crude oil. Asphaltene cannot dissolve in crude oil as single molecules, but can exist in crude oil as aggregated colloidal particles (Aurel, 2006; Fang et al., 2012; Xu et al., 2013, 2015; Yao et al., 2020; Yang et al., 2018a; Yang et al., 2018; Yang et al., 2018). It has been proved that the colloidal asphaltene particles are the natural PPDs of waxy crude oil, but its pour point depressing performance is limited. Recently, some researchers pointed out that the asphaltene could also obviously influence the efficiency of polymeric PPDs (Fang et al., 2012; Liu et al., 2015; Xu et al., 2013, 2015). Liu et al. (Fang et al., 2012; Liu et al., 2015) prepared a series of reactive PPDs and found that the asphaltene and resins can react with PPDs to form the asphaltene-resin-PPDs agglomerates. They deduced that the agglomerates could act as wax crystal nucleators and modify the process of wax crystallization, thus enhancing the rheology of crude oil. Xu and his colleagues (Xu et al., 2013, 2015) synthesized comb-type PPDs (poly maleic alkylamide-co- $\alpha$ -octadecene) with different pendants, and studied the influence of the PPDs on the crystallization of wax molecules and the rheological properties of model waxy oil. The results showed that the PPDs with small aromatic pendants or an appropriate proportion of polar/nonpolar group have the best pour point depressing effectiveness and reduce the paraffin precipitation enthalpy/temperature. They supposed that the introduction of aromatic or polar groups can facilitate the interaction between PPD molecules and resin/asphaltene to form PPD-resin/asphaltene composites, which can further improve the performance of PPDs. However, the above work only presents a hypothesis and does not provide sufficient evidence for the interaction between PPDs and asphaltene.

Lately, Yao et al. (Yao et al., 2020; Yang et al., 2018; Yang et al., 2018; Yang et al., 2018) explored the effect of asphaltene on the performance of EVA PPDs in model waxy oils by means of asphaltene adsorption experiments, micro-examination and rheological tests. The results indicated that when asphaltene or EVA are added alone, the fluidity improving efficiency of the model waxy oils is limited. However, when adding asphaltene and EVA PPDs

together, the EVA molecules can be adsorbed on the aggregated asphaltene to form composite particles, which can serve as heterogeneous nucleation templates, thus facilitate the formation of large and compact wax crystals and dramatically improving the low-temperature rheology of the model oils. The synergistic effect between asphaltene and EVA is dependent on the content of VA groups in EVA, the asphaltene content, the asphaltene polarity and the wax content, etc. However, the progress in this field is currently only at the level of model waxy oil, and whether the synergistic effect exists in real waxy crude oil is still in doubt.

The dispersion state of asphaltene has greatly influence on the synergistic effect of EVA PPDs and asphaltene. There are many factors that affect the dispersion of asphaltene, of which the existence of resins in crude oil is one of the considerable factors (Alcázar-Vara et al., 2015; Franco et al., 2015; Firoozabadi, 2010). Resins are amphiphilic molecules with relatively weak polar and small molecular weight, which can well dissolve in the oil phase (Alcázar-Vara et al., 2015; Franco et al., 2015; Juan et al., 1996). Resins are stabilizers of asphaltene, and the stability is improved by inhibiting the self-association and aggregation of asphaltene. In supplement, artificially synthesized amphiphilic molecules such as dodecylbenzene sulfonic acid and dodecyl phenol, are often used as the stabilizers of asphaltene to inhibit the deposition of asphaltene. Laurylamine (LA) is also a kind of oil soluble amphiphile molecules, some published papers have found that the LA is a flocculant of asphaltene (Fan et al., 2010; Firoozabadi, 2010; Kriangkrai et al., 2009; Sarita et al., 2013; Leon, 2001; Yang et al., 2014), but there is little academic progress on the flocculating mechanisms of LA. Is it possible to facilitate the synergistic effect of EVA PPDs and asphaltene in real waxy crude oil by small addition of LA? We consider that this question is worth studying to discover the synergistic effect between EVA PPDs and asphaltene in real crude oil.

In this paper, the mechanism of LA as asphaltene flocculant was first elucidated according to the resins/asphaltene composition analysis; then, we found that a small dosage of LA can further enhance the rheology improvement of EVA PPDs ( $100 \text{ mg kg}^{-1}$ ) for a real waxy crude oil, and the mechanism of which was expounded based on the degree of difficulty of the EVA adsorption on the aggregated asphaltene particles. The current work verified the synergistic effect of EVA PPDs and asphaltene also exists in real waxy crude oil at the first time, which has both important theoretical and practical values.

## 2. Materials and methods

### 2.1. Materials

The oil sample used here is from Qinghai Oilfield in China, which is a typical waxy crude oil. The component parameters and basic physical properties are illustrated in Table S1 of the support information file. The oil sample is rich in wax (18.46 wt %), but the contents of resins (8.64 wt%) and asphaltene (0.91 wt%) are comparatively low. The pour point and WAT of the oil sample are  $33 \text{ }^\circ\text{C}$  and  $49.0 \text{ }^\circ\text{C}$ , respectively. (Asomaning, 2003).

The LA, toluene, *n*-heptane *n*-dodecane and EVA were all acquired from Sigma-Aldrich Co., Ltd. Both LA and *n*-dodecane have a purity of 98% and the molecular structure of LA could be seen in a previous study (Yang et al., 2014). In addition, the melt index of EVA applied here is 6, which has a VA content of 28 wt%. Both the EVA and LA were first dissolved in *n*-dodecane at different mass proportions (EVA: LA = 1:0.5, 1:1, 1:2, 1:5, 1:10) to prepare a 10 wt% *n*-dodecane solution; then, the solutions were added into the oil sample. The dosage of EVA in oil sample is constant at  $100 \text{ mg kg}^{-1}$ , while the dosages of LA in the oil sample are  $50 \text{ mg kg}^{-1}$ ,  $100 \text{ mg kg}^{-1}$ ,  $200 \text{ mg kg}^{-1}$ ,  $500 \text{ mg kg}^{-1}$  and  $1000 \text{ mg kg}^{-1}$ ,

respectively. For the convenience of the following description, the compound PPDs are named as EVA-LA-1 (100 mg kg<sup>-1</sup> EVA + 50 mg kg<sup>-1</sup> LA) ~EVA-LA-5 (100 mg kg<sup>-1</sup> EVA + 1000 mg kg<sup>-1</sup> LA), respectively.

## 2.2. Methods

### 2.2.1. Rheological experiments

A rheometer (AR-G2, TA, USA) containing coaxial cylinder test device was applied to measure the rheological properties of the untreated/treated waxy crude oil. Before the rheological experiments, all oil samples were preheated at 70 °C for an hour.

**Viscoelastic test** The temperature scan in the oscillation mode was used to research the viscoelasticity of the oil samples. The viscoelastic parameters include  $G'$  (storage modulus),  $G''$  (loss modulus) and  $\delta$  (loss angle). The temperature at which  $G' = G''$  or  $\tan \delta = 45^\circ$  is known as the gelling point, which can be summarized through the curve of viscoelastic parameters in the cooling procedure. The oil samples were cooled to the laboratorial temperature at a constant cooling rate, while ensuring that the network structure formed by the wax crystals in the cooling process will not be damaged under the conditions (oscillation frequency is 1Hz, shear strain amplitude is 0.0005).

**Yield characteristic measurement** The method of continuous increase of shear rate (Souas et al., 2018) is used to measure the yield value of the oil samples: the samples were cooled statically from 70 °C to the required temperature and held for 30 min; subsequently, the yield value of the oil sample is tested and recorded by controlling the logarithmic increase in shear rate within a short period of time.

**Rheological curve test** The untreated/treated crude oil was maintained in a coaxial cylinder system for 30 min at the test temperature. Subsequently, followed by an extension of the shear rate from 1 s<sup>-1</sup> to 200 s<sup>-1</sup> over a period of 10 min, and the instantaneous apparent viscosity was recorded as a function of the shear rate at the same time.

### 2.2.2. Pour point tests

The pour point of the oil sample before and after adding the compound PPDs was measured based on the method mentioned in the China Petroleum Industry Standard SY/T0541-2009. The detailed description of the method could be found in literatures (Yao et al., 2020; Yang et al., 2018a; Yang et al., 2018c; Yang et al., 2018d).

### 2.2.3. DSC experiments

The differential scanning 821° calorimeter was used to measure the crystallization exothermic characteristics of the untreated/treated oil samples. Before the test, the temperature and heat flow of the DSC were calibrated with metal indium, and then the aluminum crucible containing 6–9 mg oil sample was placed in the sample cell of the DSC. Subsequently, the variation curve of the heat flow with temperature in a specific temperature interval, i.e. the DSC curve, was measured at the rate of 10 °C/min. The temperature at which the DSC curve started to depart from the baseline (a straight line fitted in the high temperature section) was the WAT of the oil sample (Jack, 2009).

### 2.2.4. Microscopic observation

The BX51 polarized light microscope was selected to take the polarized light micrographs of wax crystals.

### 2.2.5. Granularity test

The oil samples were added to a solution of toluene and n-heptane. To maintain the same asphaltene particle size before and

after dilution, the ratio of toluene to n-heptane was equal to the ratio of aromatic and saturated fractions of the real crude oil. The equivalent particle size of the asphaltene particles in the dispersion was then measured at 25 °C using a Mastersize 2000 laser particle sizer from Malvern Instruments Ltd, UK.

### 2.2.6. Characterization of resins/asphaltenes

Resins/asphaltenes separated from the undoped/doped oil samples were characterised by FT-IR spectrometer (Nicolet iz10, Thermol Scientific Co., USA). Separation of resins/asphaltenes from the oil samples was completed according to the method mentioned in the published paper (Lashkarbolooki and Ayatollahi, 2018).

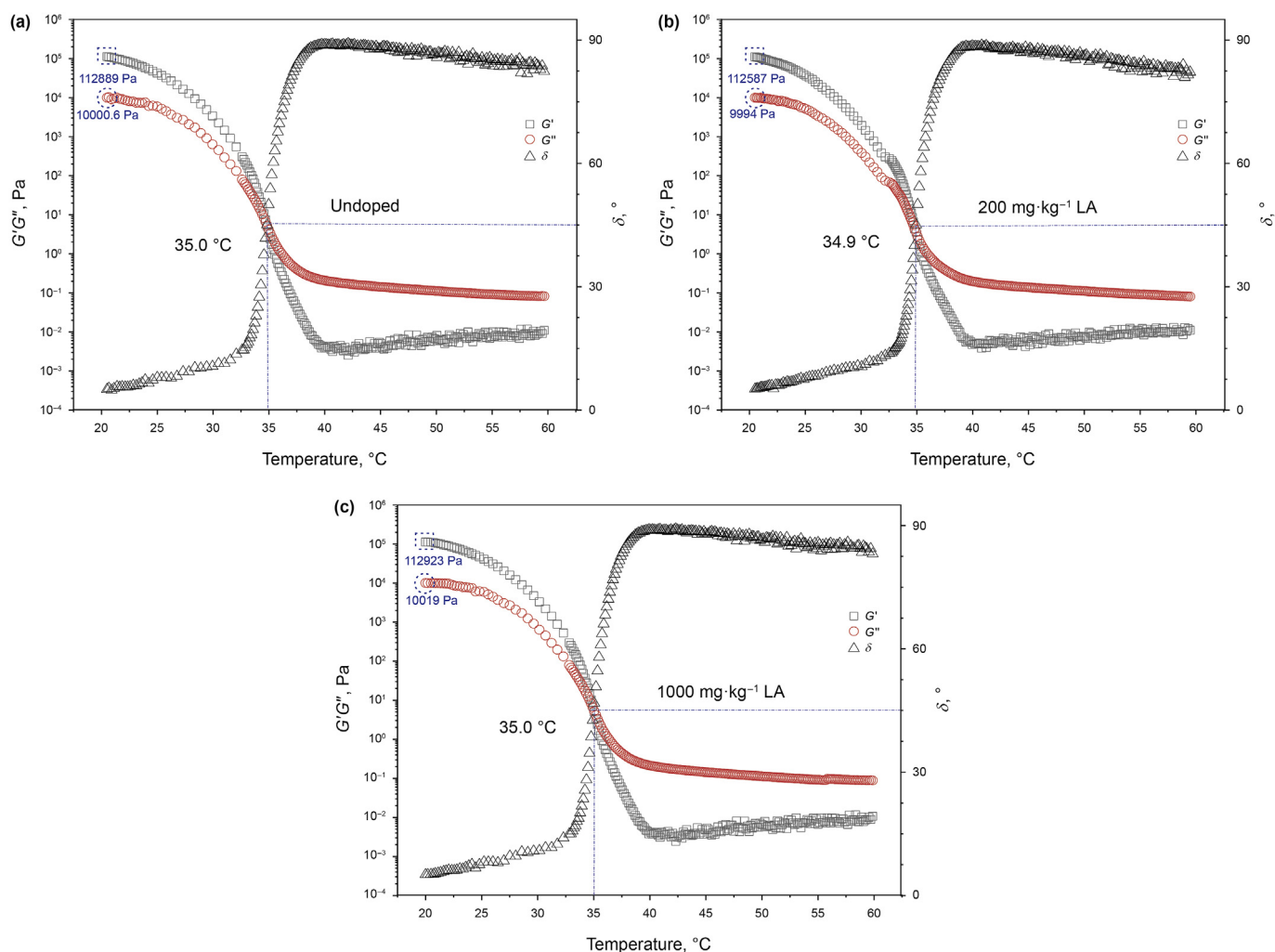
## 3. Results and discussion

### 3.1. The effect of compound PPDs on the rheology of Qinghai crude oil

#### 3.1.1. Structural development of Qinghai crude oil

The viscoelasticity test is a widespread method to measure the structural changes in crude oil. The gelation point, which is the critical temperature of oil sample from sol to gel, is one of the most considerable parameters in the viscoelasticity test. Fig. 1, Fig. 2 and Table 1 show that the viscoelasticity trend of Qinghai crude oil undoped/doped with different additives. At temperatures higher than the WAT, the properties of oil samples are hardly disturbed by the precipitated wax crystals, resulting in small values of  $G'$  and  $G''$ , and the specimen exhibits the characteristics of a viscous fluid at this temperature. In this state,  $G''$  is higher than  $G'$ , and the phase angle value is around 90°. However, as the temperature continued to decrease, the wax molecules continued to crystallize and precipitate out, resulting in both  $G'/G''$  increased, but the growth rate of  $G'$  was greater than  $G''$ . For untreated Qinghai crude oil, the intersection of the two curves occurs at 35.0 °C, which means that the gelling point of the pure oil sample is 35 °C. As the temperature continued to decrease, the elastic properties of the oil samples gradually dominated, and the  $G'/G''$  values reached 112889 Pa/10000.6 Pa respectively at 20 °C. In order to confirm the LA addition alone does not affect the viscoelasticity of the oil samples, the effects of adding 50 mg kg<sup>-1</sup>, 100 mg kg<sup>-1</sup>, 200 mg kg<sup>-1</sup>, 500 mg kg<sup>-1</sup>, 1000 mg kg<sup>-1</sup> LA were preceded. Since there is no significant difference in the viscoelasticity of the oil samples doped with 0–1000 ppm LA, to facilitate the description of the experimental results, only the 200 mg kg<sup>-1</sup> and the 1000 mg kg<sup>-1</sup> dosages were shown in Fig. 1 (b)/(c) as representatives (The others were exhibited in the "Supporting Information" (Fig. S1)). As seen in Fig. 1 (b)/(c), adding 200 mg kg<sup>-1</sup>/1000 mg kg<sup>-1</sup> LA cannot affect the  $G'/G''$  values and the gelling point obviously, which can eliminate the interference of LA on the viscoelasticity of Qinghai crude oil.

After doping 100 mg kg<sup>-1</sup> EVA into the system, the gelling point of Qinghai crude oil suddenly decreased to 29.3 °C, and the  $G'/G''$  values at 20 °C were 14463.4 Pa/2853.68 Pa (Table 1, Fig. 2), indicating that EVA PPDs have an obvious inhibitory effect on the development of crude oil viscoelasticity. Similarly, when EVA-LA-1~5 were added to the oil samples, the gelling point and  $G'/G''$  values of Qinghai crude oil were further reduced, and with the increase of LA dosage, the gelling point and  $G'/G''$  values showed a trend of first decline and then increase. When EVA-LA-1 was added, the gelling point and  $G'/G''$  values (20 °C) were 27.7 °C, 6138.37 Pa/1331.85 Pa, respectively; while the introduction of EVA-LA-3 further reduced the gelling point to 27.0 °C, and  $G'/G''$  values to 4621.16 Pa/985.528 Pa. Nevertheless, when the LA compounding ratio continued to increase, the gelling point and  $G'/G''$  both rebounded, and when doped with EVA-LA-5, the gelling point increased to 28.7 °C, and  $G'/G''$  rebounded to 10895.2 Pa and



**Fig. 1.** Viscoelasticity development of the waxy crude oil during cooling process: (a) undoped; doped with (b) 200 mg kg<sup>-1</sup> LA; (c) 1000 mg kg<sup>-1</sup> LA.

2323.75 Pa. The results indicated that compounding EVA with LA into Qinghai crude oil could synergistically affect the viscoelastic development, and with the increase of LA dosage, the synergistic effect first improved ( $LA \leq 200 \text{ mg kg}^{-1}$ ), and then slightly declined ( $LA \geq 500 \text{ mg kg}^{-1}$ ).

### 3.1.2. Yield properties

The yield value expresses the structural strength of waxy crude oil at low-temperature conditions. It generally refers to the minimum shear stress value required to transform a gelled crude oil from a gelled to a flowing state, reflecting the ability of the oil sample to maintain its solid properties. The yield value of Qinghai crude oil at 20 °C before and after dosing are presented in Fig. 3 and Table 1. After adding EVA, the yield value decreased from 1072.67 Pa to 185.02 Pa, indicating that the introduction of EVA significantly weakened the structural strength of the oil sample. When EVA-LA-1~5 were added to the crude oil, the yield value is further reduced to 66.13 Pa, 53.11 Pa, 41.68 Pa, 101.39 Pa, 134.49 Pa, respectively. Obviously, the compound PPDs can synergistically weaken the gelling structure of the oil sample. As the compounding amount of LA increases, the synergistic effect also reflects the law of first strengthening and then weakening.

### 3.1.3. Rheology curve

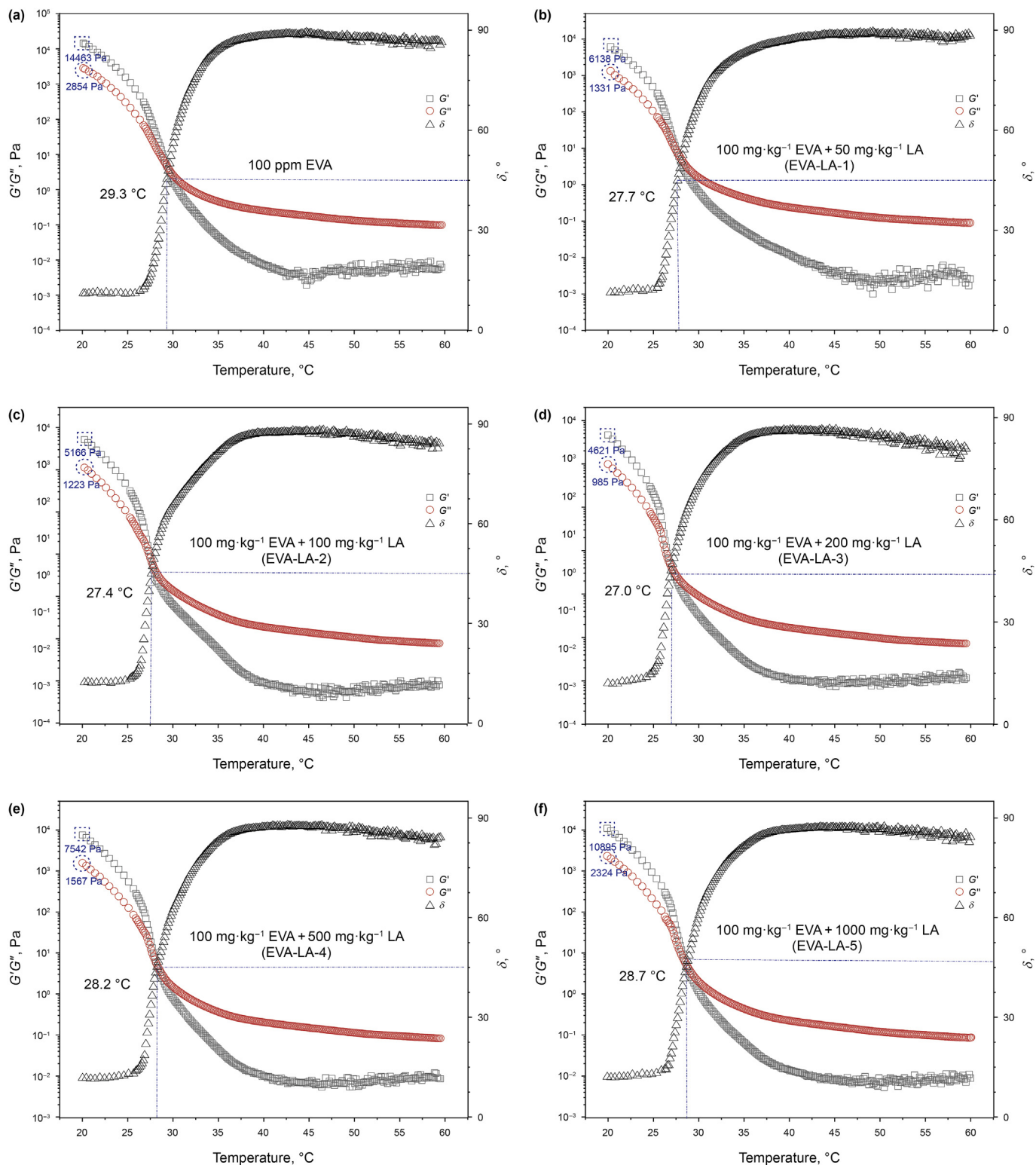
Fig. 4 illustrates the rheological curves of Qinghai oil sample before and after the addition of LA, EVA and EVA-LA-1~5. As shown

in Fig. 4, when the oil sample did not contain EVA, the addition of LA did not significantly affect the viscosity of the oil samples. After adding EVA, the apparent viscosity of Qinghai oil sample was markedly decreased. For instance, under  $10 \text{ s}^{-1}$ , the apparent viscosity of blank oil sample is 12029 mPa s, which was reduced to 1576.4 mPa s after adding  $100 \text{ mg kg}^{-1}$  EVA. After compounding EVA and LA, the apparent viscosity under  $10 \text{ s}^{-1}$  are further reduced to 637.13, 596.25, 454.28, 704.94, 983.51 mPa s. The average viscosity reduction rates of the corresponding EVA and EVA-LA-1~5 are 85.89%, 93.60%, 94.65%, 96.12%, 93.11% and 91.82%, respectively. It is apparent that when the EVA-LA-3 has the best synergistic reduction of Qinghai crude oil apparent viscosity.

### 3.2. The effects of compound PPDs on Qinghai crude oil pour point

The results of the pour point test are presented in Table 1. The pour point for blank oil sample is 33 °C, when the LA was added to the oil samples alone, no significant changes shown in pour point, but  $100 \text{ mg kg}^{-1}$  EVA could drop the pour point from 33 °C to 26 °C. However, when EVA-LA-1~5 were added to the crude oil, the pour point showed a further decrease. Among them, EVA-LA-2 and EVA-LA-3 showed the largest pour point depressing range: the pour point was further reduced by 2 °C. It can be concluded that the compound PPDs can collaboratively decrease the pour point, and the collaborative efficiency enhance and subsequently deteriorate with the growth of the LA compounding amount.





**Fig. 2.** Viscoelasticity development of the waxy crude oil during cooling process: doped with (a) 100 mg kg<sup>-1</sup> EVA. (b) EVA -LA-1; (c) EVA-LA-2; (d) EVA-LA-3; (e) EVA-LA-4; (f) EVA-LA-5.

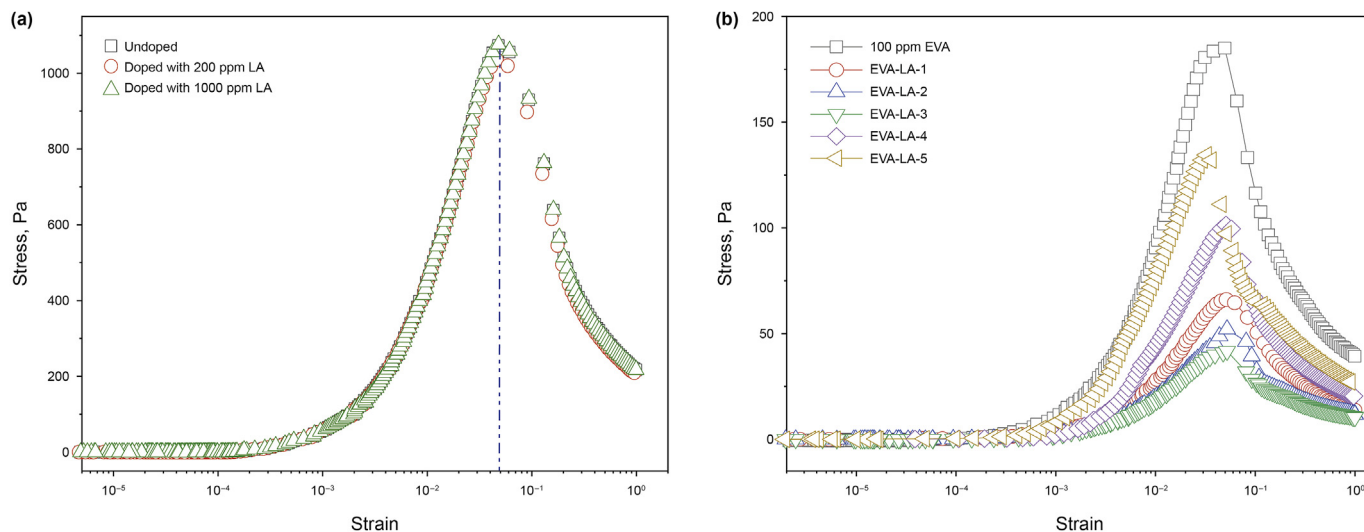
### 3.3. Exothermic characteristics of crystallization of crude oil

The crystallization exotherm curve of Qinghai crude oil with/without different additives are exhibited in Fig. 5. The WAT of crude oil without additives is 49.02 °C, which did not change significantly

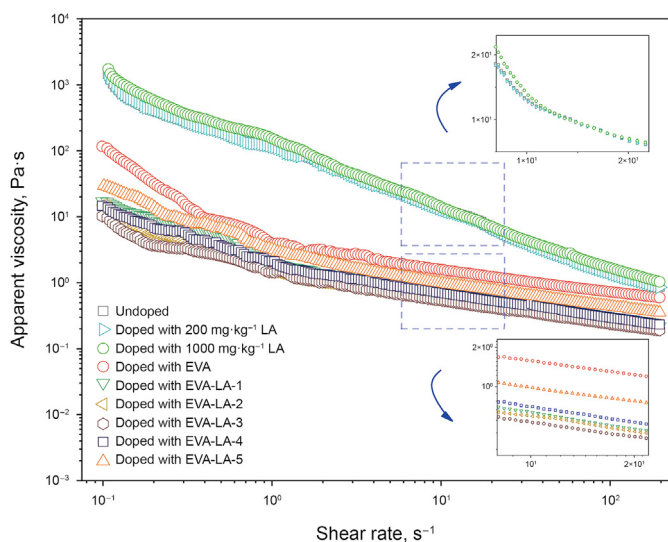
after doping with different dosages of LA alone. However, the WAT drops to 44.91 °C with the addition of 100 mg kg<sup>-1</sup> EVA. The introduction of EVA PPDs can enhance the critical nucleation radius of wax molecule and make the wax crystals effectively soluble into the oil phase (Yang et al., 2017; Yang et al., 2018a; Yang et al., 2018c;

**Table 1**  
The pour point, gelling point,  $G'/G''$  and yield value at 20 °C of the Qinghai crude oil undoped/doped with EVA or EVA-LA-1–5.

Additives	Pour point, °C	Gelling point, °C	$G'$ , Pa	$G''$ , Pa	yield value, Pa
Undoped	33	35.0	112889	10000.6	1072.67
200 mg·kg <sup>-1</sup> LA	33	34.9	112587	9993.86	1035.61
1000 mg·kg <sup>-1</sup> LA	33	35.0	112923	10001.9	1076.19
EVA	26	29.3	14463.4	2853.68	185.02
EVA-LA-1	25	27.7	6138.37	1331.85	66.13
EVA-LA-2	24	27.4	5166.46	1223.10	53.11
EVA-LA-3	24	27.0	4621.16	985.528	41.68
EVA-LA-4	25	28.2	7542.82	1566.00	101.39
EVA-LA-5	26	28.7	10895.2	2323.75	134.49



**Fig. 3.** The yield behavior of the waxy crude oil with different additives at 20 °C.



**Fig. 4.** Flow curves of the waxy crude oil undoped/doped with different additives at 20 °C.

Yang et al., 2018d). Which significantly decrease the WAT of crude oil. Nevertheless, after adding the compounding PPDs EVA-LA-1~5 to the Qinghai oil samples, the WAT started to show a slight recovery, from 45.17 °C for EVA-LA-1, to 45.42 °C for EVA-LA-2, and then to 45.68 °C for EVA-LA-3. However, it is strange that when the

LA compounding amount continues to increase, the WAT falls back: it drops to 45.40 °C for EVA-LA-4 and 45.06 °C for EVA-LA-5. Since polymer PPD molecules can adsorb onto the asphaltenes suspended in the oil phase to form polymer/asphaltene composite particles, these particles can become the nucleation template of wax molecules and enhance the WAT (Yang et al., 2018d), we speculate that the introduction of LA will affect the crystallization template role of the composite particles, leading to the change of WAT of crude oil.

### 3.4. Microscopic observation

The crystal morphology of unpolarized/polarized wax of undoped/doped with LA, EVA, EVA-LA-3 or EVA-LA-5 Qinghai crude oil at 20 °C are shown in Fig. 6. For untreated crude oil (Fig. 6a), the wax molecules are precipitated by asphaltene as nucleation sites (Machado and Lucas, 1999; Lima et al., 2009; Passade-Boupatt et al., 2018; Yang et al., 2018; Yang et al., 2018; Yang et al., 2018). The wax crystals precipitated out of undoped Qinghai crude oil are very fine (the size is generally below 1 μm) and irregularly arranged, which have huge specific surface area and can be distributed throughout the oil system. Meanwhile, the fine wax crystals lap together to form a three-dimensional mesh mechanics structure, encapsulating a large quantity of liquid oil in it and significantly reduces the low-temperature fluidity of crude oil. When LA was doped alone, the wax crystal morphology does not show noticeable changes, and only a small number of small wax crystal aggregates appear in the field of view. Although asphaltenes are

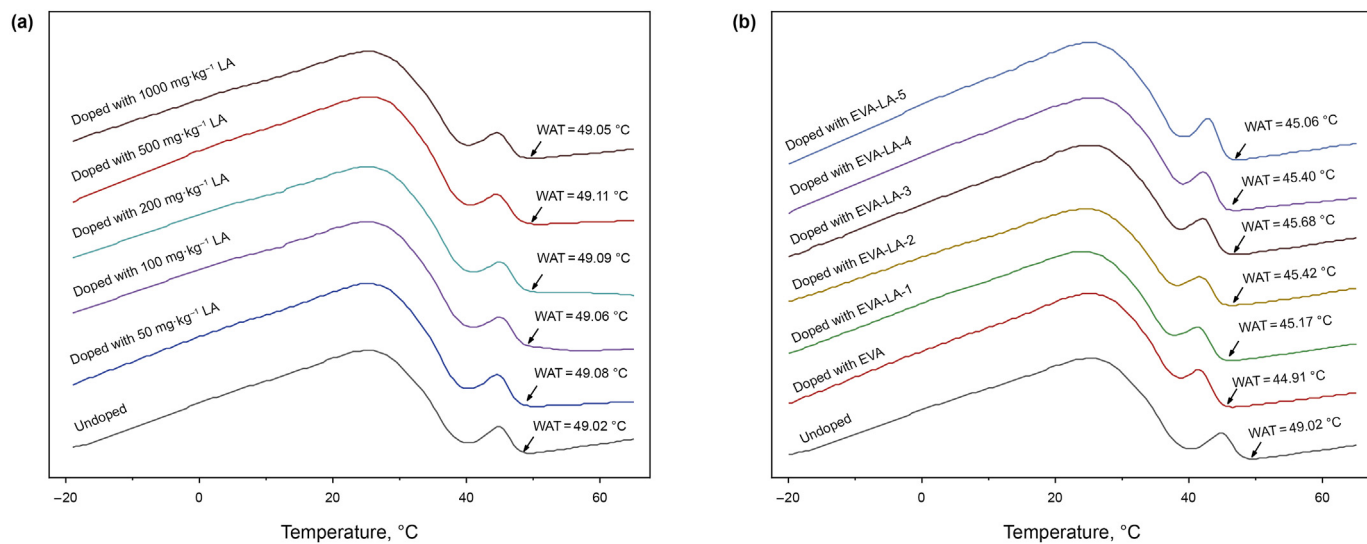


Fig. 5. DSC curves of the waxy crude oil undoped/doped with LA, EVA and EVA-LA-1-5.

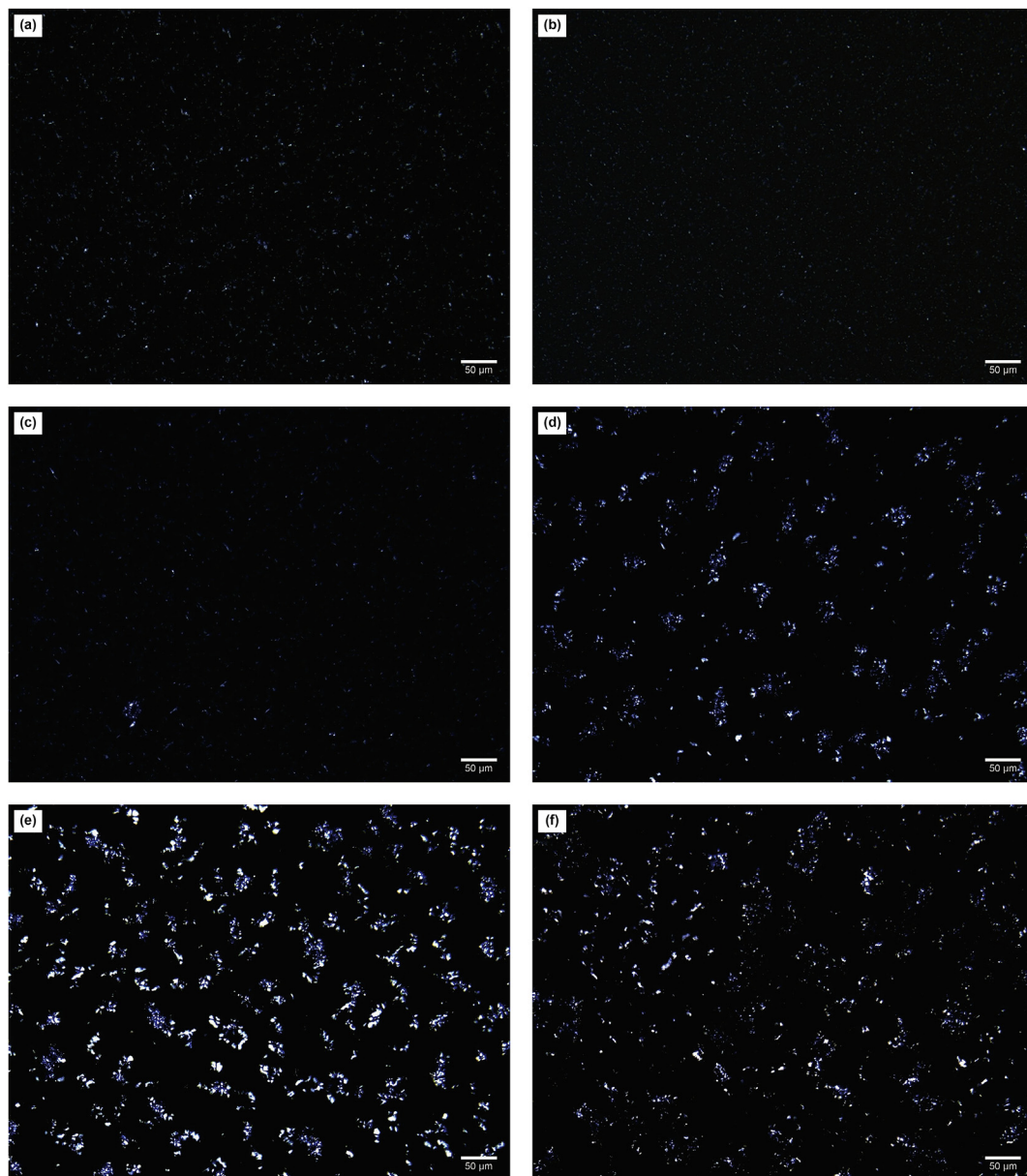


Fig. 6. Polarized-light microscopic images of the waxy crude oil at 20 °C: (a) undoped, (b) 200 mg·kg<sup>-1</sup>LA, (c) 1000 mg·kg<sup>-1</sup>LA, (d) EVA, e EVA-LA-3, f EVA-LA-5.



nucleation sites in the crystallization process of crude oil paraffin, the effect of LA on the dispersion state of asphaltenes in the experimental dosing range was not sufficient to significantly change the low-temperature rheology of Qinghai waxy crude oil.

After adding 100 mg kg<sup>-1</sup> EVA to the blank oil sample (Fig. 6d), since the PPDs can form composite particles with asphaltene, it becomes a nucleation template for wax crystals (Yang et al., 2018c), resulting in wax crystal flocs with relatively large size and high degree of aggregation starting to appear in the field of view, which improved the macroscopic rheology to some extent, but the compactness of wax crystals was poor, and there were plenty of fine wax crystals in the field of view. However, when the compound PPD EVA-LA-3 is doped into the oil phase (Fig. 6e), the appearance of the precipitated wax crystal aggregates is relatively regular, the degree of wax clustering is significantly increased, and the quantity of irregular powder-like wax crystals is notably reduced; but when the amount of LA compound further increased (Fig. 6f), although a larger wax crystal flocs appeared, their degree of clustering became significantly worse (easier to observe in polarized-light microscopic images), but some fine wax crystals appear in the field of view. EVA molecules can adsorb onto the surface of asphaltene particles, but the adsorption process is competitive with other components (e. g. resin) in the crude oil. It is speculated that the doping of moderate amount of LA will reduce the disturbance of other components to the formation process of composite PPDs, which will benefit more EVA molecules to combine with asphaltene particles, leading to the formation of more tightly wax agglomerates in the field of view. However, the introduction of excessive LA causes the asphaltenes to agglomerate, reducing the adsorption sites of EVA, leading to a reduction in the quantity of EVA adsorption on asphaltene surfaces, which causes a small deterioration in the effectiveness of EVA in improving the low-temperature rheology of Qinghai crude oil.

### 3.5. Granularity test

The particle size distribution of asphaltenes in undoped/doped oil samples are shown in Fig. 7 and their average equivalent particle size are listed in Table 2. The following analysis can be performed from the data in Fig. 7 and Table 2: When only LA was present in the oil sample, the average equivalent particle size of the asphaltenes was not significantly affected at low doses (from 183.2 nm to

**Table 2**  
Average equivalent particle size of asphaltene in crude oil.

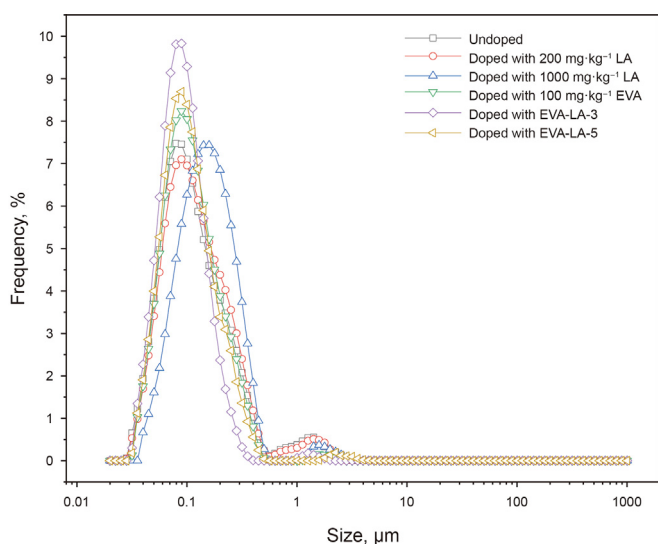
Additives	Average equivalent particle size, nm	Reduction ratio, %
Undoped	183.2	
EVA	139.2	24.01%
200 mg·kg <sup>-1</sup> LA	181.3	
EVA-LA-3	109.2	39.75%
1000 mg·kg <sup>-1</sup> LA	198.9	
EVA-LA-5	138.7	30.29%

181.3 nm), whereas the average equivalent particle size of asphaltene increased obviously (from 183.2 to 198.9 nm) when the dosage was raised 1000 mg kg<sup>-1</sup>, indicating a significant deterioration of its stability. If LA is interacting directly with asphaltene and influencing its dispersion state, then the average equivalent particle size should change proportionally with increasing dosage. However, the experimental results point to a plateau with increasing LA amount, suggesting that LA affects the dispersion of asphaltene indirectly by interacting with other substances in the oil phase.

In addition, the average equivalent particle size of asphaltenes all showed different degrees of reduction when EVA was present in the system. This phenomenon suggests that EVA has the function of stabilizing asphaltenes, which is consistent with the findings of previous studies (Yao et al., 2020; Yang et al., 2018a; Yang et al., 2018c; Yang et al., 2018d). However, the reduction effect of EVA on the stability asphaltenes showed significant differences depending on the amount of LA compounding. Among them, oil sample with EVA-LA-3 has the smallest average equivalent diameter (109.2 nm) and the highest reduction rate (39.75%), indicating that its dispersion in the oil phase was the most excellent at this time. Since EVA can adsorb on the asphaltene surface and enhance its dispersion stability, it can be speculated that compounding with low dosage of LA can enhance the adsorption of EVA on the asphaltene surface. However, when the quantity of LA compounded was too high, it would lead to destabilization of asphaltene particles, which in turn would increase the equivalent diameter of asphaltene particles (139.7 nm). This is shown by the significantly weaker effect of EVA-LA-5 on the mean asphaltene particle size than EVA-LA-3.

### 3.6. Mechanism discussion

The results of pour point experiments and macro rheology tests show a similar phenomenon: when only LA is present in the system, there is no obvious influence on the macroscopic rheology of oil sample; however, when LA was compounded with EVA, the modification effect on the oil samples tended to be enhanced and then weakened with the increase of LA compounding ratio. Combining the test results of DSC in Fig. 5 and the measurement data of the granularity tests (Fig. 7), we proposed the following hypothesis: resin in crude oil can play a role in stabilizing asphaltene (Ren et al., 2017a), there is a threshold value for the dispersion of asphaltene by resin. The resin within the threshold is adsorbed on the surface of the asphaltene or embedded in the asphaltene lamellae to disperse the asphaltenes through  $\pi$ - $\pi$  interaction, while the fraction beyond the threshold is unable to stabilize the asphaltenes and disturbs adsorption of PPD molecules on the asphaltene surface. Nevertheless, the introduction of a small amount of LA will interact with the acidic groups of the resins beyond the "threshold", and introduce alkyl chains on the surface of resin at the same time, resulting in the increase of non-polarity on the surface of resin and weakening its interaction force with the polar asphaltenes. However, when the dosage of LA is too excessive, the LA will affect the dispersion of asphaltenes by resins under the



**Fig. 7.** The equivalent particle size distribution of asphaltene in experimental oil undoped/doped with different additives.



"threshold", which will make the asphaltene particles less stable, resulting in fewer adsorption sites and lower adsorption of EVA on asphaltenes, and then weakening the improvement effect of EVA PPDs on waxy crude oil (Fig. 8).

To confirm the above hypothesis, Fourier infrared spectroscopy tests were carried out on undoped/doped Qinghai crude oil resin. Previous studies have suggested that the results of FT-IR spectroscopy for obtaining structural information of resin molecules are relatively stable (Bosch et al., 2006). The test findings are shown in Fig. 9. For resin (Fig. 9a), the differences between the two before and after the addition of  $1000 \text{ mg kg}^{-1}$  LA are mainly reflected near the absorption peaks at wavelengths of  $3380 \text{ cm}^{-1}$ ,  $2848 \text{ cm}^{-1}$ ,  $1461 \text{ cm}^{-1}$ ,  $1375 \text{ cm}^{-1}$ ,  $1220 \text{ cm}^{-1}$ , and  $928 \text{ cm}^{-1}$ . It can be seen that for undoped oil sample resin, there are no absorption peaks existed, while a moderately intense absorption peak appears in  $3600\text{--}3100 \text{ cm}^{-1}$  after adding  $1000 \text{ mg kg}^{-1}$  LA, which belongs to the  $\text{--NH}$  stretching vibration of aromatic secondary amines, directly proving the new presentation of amine groups in the resin. The  $\text{--CH}_2$  stretching vibration peaks are around  $2925 \text{ cm}^{-1}$  and  $2855 \text{ cm}^{-1}$ , but the frequency of the  $\text{--CH}_2$  stretching vibration decreases by  $5\text{--}7 \text{ cm}^{-1}$  in the ordered long alkyl chains, suggesting that new long alkyl chains were introduced into doped resins, while the significant increase in the intensity of the absorption peaks at  $1374 \text{ cm}^{-1}$  and  $1461 \text{ cm}^{-1}$  proves the newly added  $\text{--CH}_2$  is connected to a strong electronegative group. At the same time, the absorption peaks at  $1220 \text{ cm}^{-1}$  and  $928 \text{ cm}^{-1}$ , which represent the stretching vibration of the anhydride, disappeared in the resin of doped oil sample. Taken together, it can be deduced that the addition of LA to the system reacts with the Qinghai crude oil resins and introduces strong polar amine group into the resin molecules. Nevertheless, no significant changes were observed in the infrared spectrum of asphaltene (Fig. 9b).

In addition, the mechanism of LA flocculating asphaltene can also be obtained: LA does not destabilize asphaltene by direct role on asphaltene, but by acid-base interaction with resin, which stabilizes asphaltene in the oil phase, the highly electronegative amine group is embedded in the resin macromolecule, and the non-polar alkyl side chains are exposed on the outside of the molecule to enhance the non-polarity of resin. The occupation of polar sites and the enhancement of non-polarity lead to the weakening of van der Waals forces between resin and the highly polar asphaltene molecules, which further leads to the weakening of its ability to disperse asphaltenes and the enhancement of the tendency of self-association, resulting in the destabilization of asphaltenes.

#### 4. Conclusion

In this paper, the effects of the dosage of LA on the synergistic effect between EVA PPDs and asphaltenes were investigated by rheological tests, microscopic observations, DSC measurement and asphaltene precipitation experiments. The appropriate amount of LA could improve the improvement effect of the EVA PPDs on crude oil, and the tendency of the enhancement strengthened and then weakened with the increase of LA dosage (the best effect is achieved when the amount is 200 ppm). We recommend that the small amount of LA will interact with the resin and weakening its interaction force with the polar asphaltenes. The reserved sites on asphaltenes will facilitate the adsorption of EVA molecules to it and improve the modification effect of EVA/asphaltenes composite particles. But when the LA is excessive, it could agglomerate the asphaltenes and lead to a slight deterioration in the rheology of oil samples. Meanwhile, the mechanism of LA destroying asphaltenes dispersion stability is proposed, that is, LA weakens the polar force between resins and asphaltenes by occupying the polar adsorption

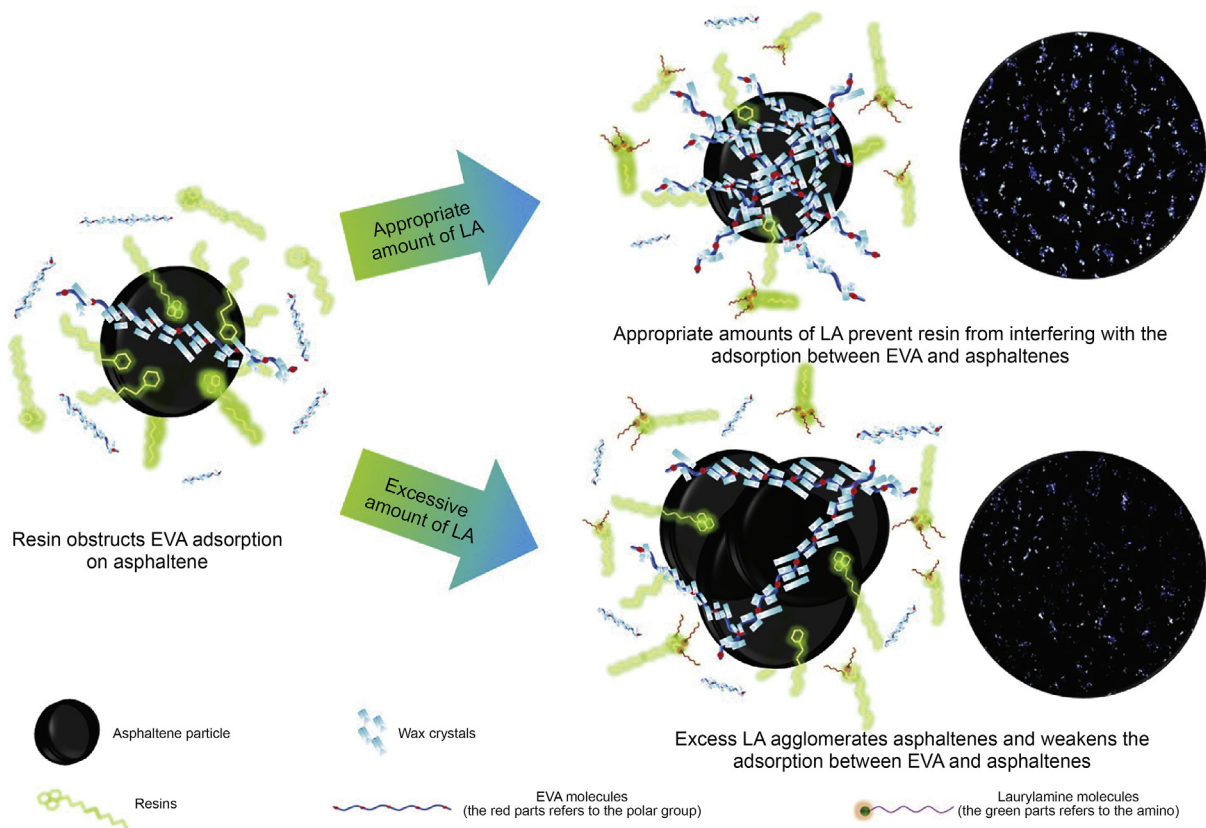


Fig. 8. Mechanism illustration of the synergistic effect of EVA and LA for improving the flow behavior of Qinghai crude oil.

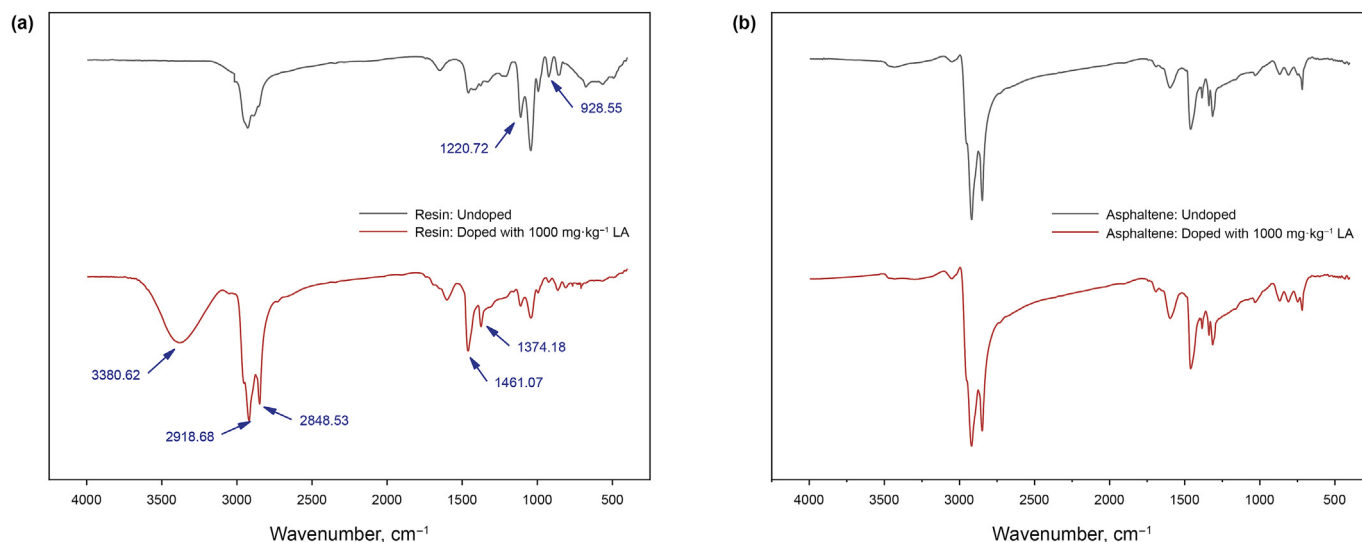


Fig. 9. The FT-IR spectra of the resins (a) and asphaltenes (b) separated from the waxy crude oil undoped/doped with 1000 mg kg<sup>-1</sup> LA.

sites of resins, which obstructs the dispersion function of resins on asphaltenes and leads to the destruction of asphaltenes stability. The above study demonstrates that there is still a synergistic effect of PPDs and asphaltenes in real crude oil system and this effect can be influenced by resin, which offers innovative ideas for the improvement of the rheological properties of crude oil.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petsci.2022.04.002>.

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