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The influencing factors of evaporation residue of emulsified modified asphalt to optimize the environmental adaptability

Yan Lin [a], Chengduo Qian [b], Jingtao Shi [c], Yuzhen Zhang [a], Shisong Ren [d], Guozhi Nan [a], Xiangjun Kong [e,*], Weiyu Fan [a,*]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, PR China
[b] Shandong Hi-Speed Group Innovation Research Institute, Jinan 250101, PR China
[c] PetroChina Fuel Oil Co. Ltd., Research Institute, Beijing 100195, PR China
[d] Delft University of Technology, Stevinweg 1, 2628, CN, Delft, the Netherlands
[e] Weifang University, Weifang 261061, PR China

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ABSTRACT

Compared with traditional asphalt, emulsified asphalt occurs to be a better low-temperature usability and environmental adaptability, which can reduce environmental pollution and energy consuming during road construction. The low-temperature ductility is a very important indicator to evaluate the environmental adaptability of emulsified asphalt. However, the relevance between microstructure and low-temperature ductility of modified asphalt is still rarely reported. Herein, we reported the first successful unfolding of the microscopic mechanism of ductility attenuation of the modified emulsified asphalt by combining experiments and characterization: Emulsifiers and additives had greater influence on the low-temperature ductility. Anionic and cationic emulsifiers had the similar ductility loss. Adding a non-ionic emulsifier OP-10 could be a solution to improve the ductility. The effect of the temperature change occurred less significant compared to the pH evolution of surfactant solution. The grey relation entropy (GRE) analysis revealed that the emulsifier structure (C/H ratio) would be the most important factor to affect the low-temperature ductility. The macro, micro and nano scales of modified emulsified asphalt were correlated, revealing in-depth that the aggregation and inter-chains interaction of styrene-butadiene-styrene (SBS) were the internal mechanism leading to the ductility loss. The change of glass transition temperature (Tg) was proposed to correlate the microstructural factor with the ductility. Moreover, the combination of ductility test and bending beam rheometer (BBR) test could be an effective way to evaluate the low-temperature performance of asphalt.

1. Introduction

Asphalt is the residue of crude oil refining, containing aromatic hydrocarbons, benzene, naphthalene, pyridine, etc., which may cause asphalt to be harmful to the environment under traditional heating operations [1–7]. Compared with traditional hot asphalt, emulsified asphalt was intensively adopted to reduce environmental pollution and energy consuming during road construction, which owned better low-temperature usability and environmental adaptability [8–11]. Recently, the increasing requirements of waterproofing infrastructure, as well as the progresses of road slurry sealing and micro-surfacing have greatly promoted the development of emulsified asphalt [12–14].

However, some environmental factors, such as temperature, ultraviolet rays, water, etc., can accelerate the deterioration of emulsified asphalt's adaptability [15–17]. Especially, the low temperature in cold regions will cause serious cracks and pavement diseases, which affects performance and lifespan of pavement [18–20]. Therefore, the emulsified asphalt used in pavement maintenance in cold regions needs to overcome these challenges at low temperature. The low-temperature ductility is one important indicator of the toughness and low-temperature performance of asphalt materials. Especially when applied in low-temperature environment, the ductility index is required very strictly. Therefore, it is very meaningful to explore the effect of the emulsification on promoting low-temperature ductility to improve environmental adaptability.

With the rapid development of road traffic, ordinary asphalt can no

* Corresponding authors.
E-mail addresses: kxj@wfu.edu.cn (X. Kong), 15853256892@139.com (W. Fan).

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Table 1
The basic properties of Shuanglong AH-70 modified asphalt.

Items	Measured values	Specifications
Penetration(25 °C)/0.1 mm	93	GB/T 0604
Softening Point/°C	58.8	GB/T 0605
Ductility(5 °C)/cm	47.1	GB/T 0606
Storage stability/°C	0.1	GB/T 0661

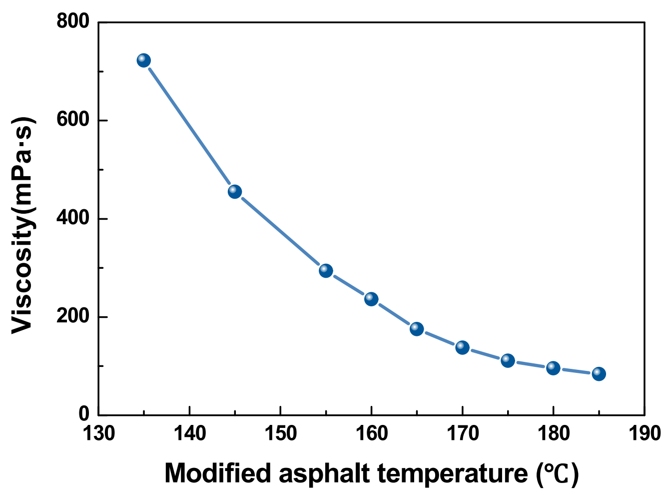

Fig. 1. The viscosity-temperature curve of Shuanglong AH-70 modified asphalt.

longer meet the increasing requirements on pavement performance and environmental adaptability [21–24]. Adding polymers and additives is a main method to improve the low-temperature performance of asphalt [25–28]. At present, polymer SBS is one of the most popular asphalt modifiers [29–32]. Using modified emulsified asphalt for paving and repairing can reduce or even eliminate pavement diseases and reduce maintaining costs [33,34]. After the modified emulsified asphalt is demulsified, the final performance is still determined by the modified asphalt (or namely evaporation residue) [35,36], which is used to evaluate the road performance of the modified emulsified asphalt [37].

In previous reports, the low-temperature ductility of ordinary emulsified asphalt could be affected by emulsifiers, additives and emulsification conditions [38–41]. Song et al. revealed that the emulsifier structure could obviously affect the ductility index of asphalt [38]. Hou et al. indicated that the evaporation residue of emulsified asphalt exhibited higher sensitivity on temperature, resulting in lower elastic recovery, poor anti-cracking and storage stability. Especially low-temperature ductility, the value of ductility attenuation (difference in ductility before and after emulsification) could even be as high as 40 cm [39]. Fan et al. found that the stabilizer could significantly reduce the ductility of emulsified asphalt, which was mainly due to the re-fusion of asphalt particles after demulsification [40]. Although the influence of low-temperature ductility of emulsified asphalt have been studied as above mentioned, there are still many challenges: Firstly, there was a lack of systematic research on the influencing factors of low-temperature ductility of emulsified modified asphalt. Secondly, most of the current researches were aimed at ordinary emulsified asphalt. The effect of structural changes on modified emulsified asphalt before and after emulsification was rarely considered. Lastly, there was a lack of microscopic characterization to explore the mechanism of ductility attenuation of modified emulsified asphalt. Therefore, the influence of the emulsification process on the low-temperature ductility needs to be further studied, which can help establish the relation between the microstructure and the macroscopic low-temperature ductility of modified emulsified asphalt.

Herein, we reported the first successful unfolding of the microscopic mechanism of ductility attenuation of the modified emulsified asphalt by combining experiments and characterization. To explore the influence of emulsification factors on the low-temperature ductility, 9 kinds of typical emulsifiers and 3 kinds of common additives were selected as raw materials. Furthermore, the fluorescence microscopy (FM), Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) results revealed the origin of ductility attenuation, which was caused by aggregation and the inter-chains interaction of SBS. Therefore, the microstructure and low-temperature ductility of emulsified modified asphalt was correlated. This study will provide scientific guidance for emulsifier design and feasible emulsification methods for advanced modified asphalt.

2. Materials and methods

2.1. Materials

Shuanglong AH-70 modified asphalt was used as raw material [named according to Technical Specifications for Construction of Highway Asphalt Pavement (JTG F40)]. The linear SBS copolymer (T6302H) was provided by Dushanzi Petrochemical Co., Ltd. The furfural extract oil (ZR-30) was purchased from China National Petroleum Corporation. The stabilizer (HAD) was prepared by the laboratory. The basic properties of Shuanglong AH-70 modified asphalt were presented in Table 1. The Brinell rotational viscosity and temperature curve was shown in Fig. 1.

Cationic polyamine emulsifier (PMC), long chain alkyl imidazoline (MAK-1), cycloalkyl imidazoline (MAK-2), gemini imidazoline quaternary ammonium salt (GIQA) were synthesized by the laboratory. Hydroxyethyl cellulose (HEC) and sodium carboxymethyl cellulose (CMC) were provided by Medwiswick Co., Ltd. Octadecyl trimethyl ammonium chloride (1831), sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (SDSN), alkylphenol ethoxylates (OP-10), and calcium chloride ($CaCl_2$) were provided by Sinopharm Chemical Reagent Co., Ltd. Alkali lignin (AL) was provided by Shanghai Longfu Technology Co., Ltd.

2.2. Preparation of modified emulsified asphalt

Shuanglong AH-70 modified asphalt was prepared by high shear method. The SBS (3.0 wt%), extract oil ZR-30 (2.0 wt%) and stabilizer HAD (0.3 wt%) was added to the base asphalt under high shearing (4000 rpm) at 170 °C for 30 min. The sample was then transferred to a stirrer for 3 h, at 165 °C and 1200 rpm. The high sheer colloid mill (DALWORTH DLP-005 V) was used as an emulsifying device. The mill and pipeline were heated to 175 °C and 110 °C, respectively. Then, the modified asphalt and surfactant solution were poured into tanks, and preheated to 165 °C and 60 °C, respectively. The colloid mill was turned on, and then the preheated surfactant solution and modified asphalt were poured into the colloid mill for stirring and shearing. During the emulsification, the pressure in the circulation pipeline was controlled to be constant at 20 psi. The mass ratio of asphalt/water was 60: 40, the emulsifier content was 1.5 wt% (based on the mass of emulsified asphalt). The flow chart of preparation of modified emulsified asphalt was shown in Fig. 2.

2.3. Preparation of evaporation residue of modified emulsified asphalt

First, 300 g of the modified emulsified asphalt was put in a weighed beaker, stirred and heated at a temperature below 100 °C to evaporate part of the water. After heating to 100 °C, the temperature was kept for 3 min. Then, the evaporation residue was spread evenly on the silica gel plate, and the silica gel plate was put in an oven at 60 °C for 1 h. After the silica gel plate was taken out and cooled to room temperature, the residue was scraped and placed in a beaker. The weighed residue was

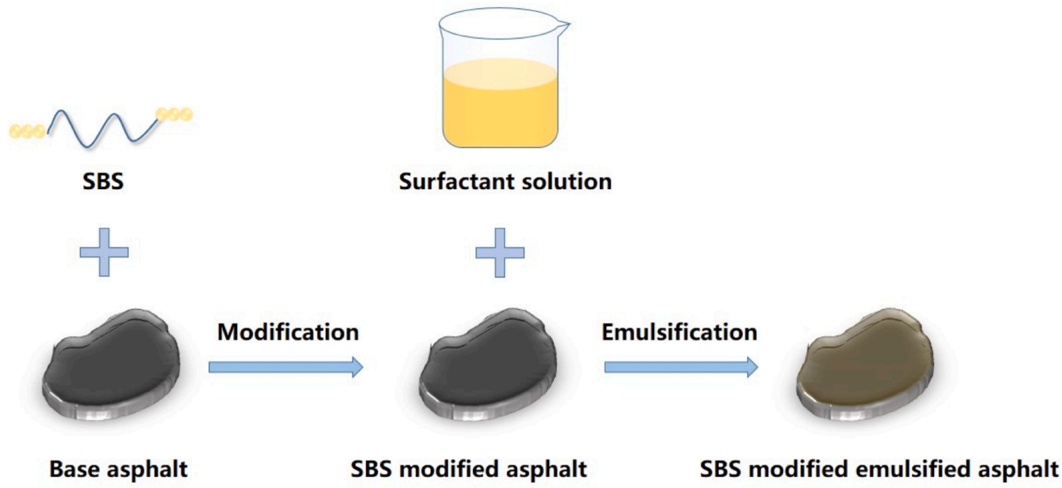

Fig. 2. Flow chart of preparation of modified emulsified asphalt.

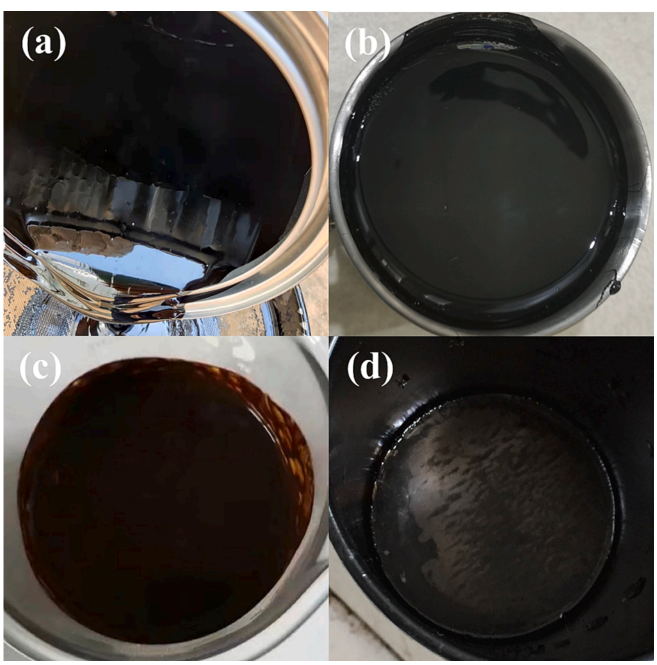

Fig. 3. Appearances of (a) base asphalt (b) SBS modified asphalt (c) SBS modified emulsified asphalt (d) evaporation residue of modified emulsified asphalt.

placed in an oven at 155 °C until it has fluidity. Then, the residue was stirred continuously at 155 °C until the residue surface was smooth and flat without bubbles, the temperature was increased and kept at 160 °C for 1 min. The appearances of base asphalt, SBS modified asphalt, SBS modified emulsified asphalt and evaporation residue were shown in Fig. 3.

2.4. Test methods

2.4.1. Properties of modified asphalt

Penetration, ductility, softening point, storage stability and Brinell rotational viscosity were analyzed according to GB/T0604, GB/T0605, GB/T0606, GB/T0661 and GB/T0625, respectively.

The test method of ductility at 5 °C was as follows: the heated asphalt was poured slowly into the mold until the asphalt was slightly above the mold. The sample was cooled at room temperature for 1.5 h, and then the asphalt above the mold was scraped off with a hot scraper. The sample was placed in the water tank of the ductility measuring instrument at 5 ± 0.1 °C for 1.5 h. After the sample was placed on the slide plate, the test button and circulated water were turned on. When the sample was pulled off, the value on the scale was the ductility at 5 °C.

2.4.2. Bending beam rheometer

The ductility test and the bending beam rheometer (BBR, Cannon) test can simultaneously evaluate the low-temperature performance of asphalt. The former reflects the low-temperature plastic deformation ability of asphalt, and the latter reflects the low-temperature modulus and relaxation capacity of asphalt. In general, a lower creep stiffness (S-value) indicates less stiffness of asphalt, while a higher relaxation rate (m-value) indicates faster relaxation of stress. The lower S-value and higher m-value are desirable for asphalt to resist the cracking at low temperature. It is one-sided to evaluate the low-temperature properties of asphalt by a single S-value or a single m-value. Therefore, $k = S/m$ is defined as the index to evaluate low-temperature performance, which takes asphalt modulus and relaxation capacity into consideration [42]. At the same temperature, the decreasing of k value indicates better low temperature anti-cracking and relaxation capacity of asphalt. To guarantee superior low-temperature performance of asphalt, the American Superpave performance specification stipulates a maximum S-value of 300 MPa and minimum m-value of 0.3. The BBR test was carried out according to the specification AASHTO T313-12.

2.4.3. Differential scanning calorimetry

The essence of modified asphalt is high polymer. The glass transition temperature (Tg) can be used to characterize the low-temperature performance of high polymers. The Tg refers to the temperature at which the glass state changes to the highly elastic state. When the temperature reaches Tg, the properties of polymer materials change significantly. For modified asphalt, it is a transition from better flexibility and plasticity to easy cracking and brittleness. The lower Tg indicates better fluidity and deformability of the modified asphalt at low temperature, which can effectively reduce cracking. Therefore, the low-temperature performance of modified asphalt can be effectively characterized by the Tg obtained from DSC. Herein, the Tg (the change in molecular chain flexibility/inter-chains interaction) was used to compare the low-

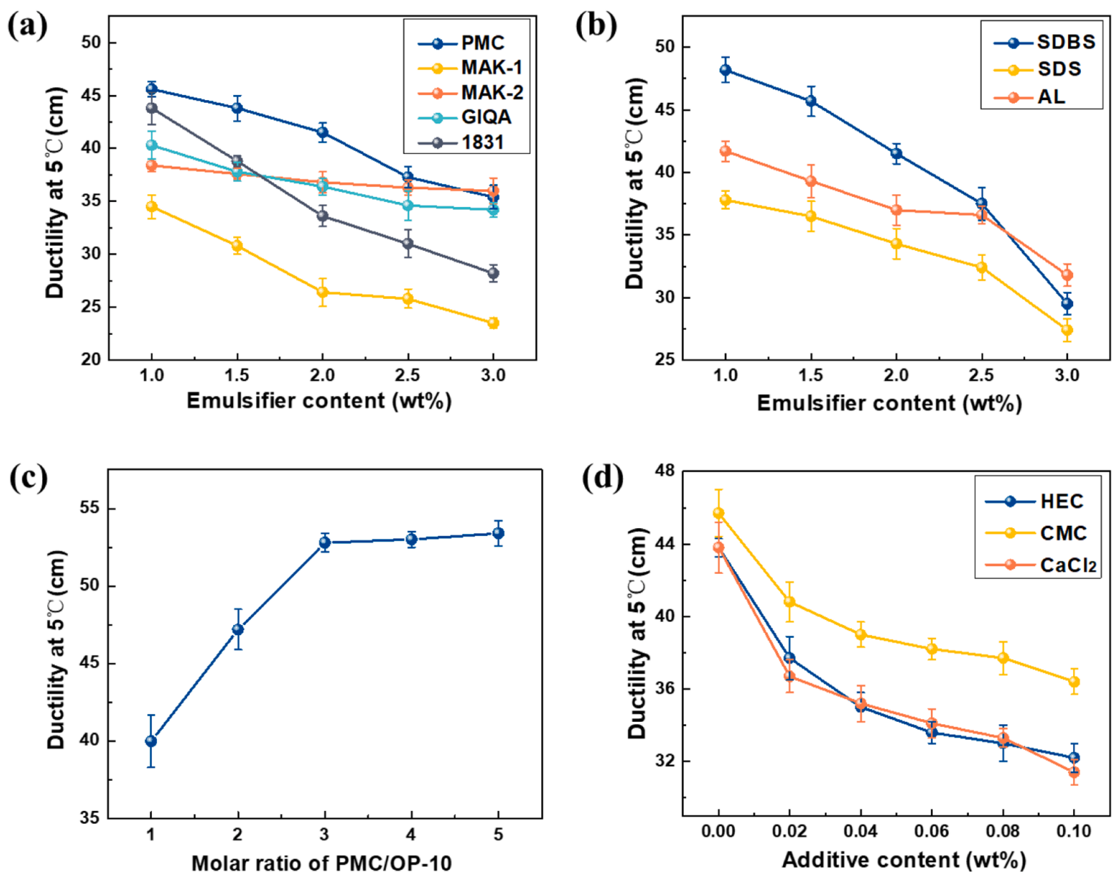

Fig. 4. The effect of (a) content of cationic emulsifier (b) content of anionic emulsifier (c) molar ratio of PMC/OP-10 (d) additive (PMC + HEC, SDBS + CMC, PMC + $CaCl_2$) content on the ductility at 5 °C of evaporation residue of modified emulsified asphalt.

temperature ductility of the modified asphalt before and after emulsification. The DSC was performed on a NETZSCH DSC 204 F1 calorimeter. The DSC analysis parameters were as follow: the heating rate was 10 °C·min^{-1}, the temperature range was −50 °C~150 °C, and the flow rate of nitrogen was 20 mL·min^{-1}.

2.4.4. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is one of the most common characterization methods to study the chemical structure of asphalt and polymers. To explore the mechanism of ductility loss before and after emulsification, the Nicolet iS10 Fourier Transform Infrared Spectrometer was employed to analyze the functional group changes of SBS during emulsification. The asphalt was evenly and thinly coated on KBr salt flakes to obtain FT-IR spectra at wavenumber between 4000 cm^{-1} and 400 cm^{-1} (coating method).

2.4.5. Fluorescence microscopy

The microstructure of SBS is typically observed by Fluorescence microscopy (FM) due to the different fluorescence properties of asphalt and polymer. Herein, the FM-400C fluorescence microscope was used to compare the morphology and distribution of SBS in asphalt before and after emulsification. During sample preparation, the asphalt sample was heated to a flowing state to drop onto a glass slide and then gently covered by a cover-slip. The sample was placed in an oven at 163 °C for 2 min, then taken out and cooled. The microscopic distribution of SBS before and after emulsification could be observed under 400 times magnification.

2.5. Grey relation entropy analysis

Grey relation entropy analysis is a statistical analysis method for multi-factor systems to find the relevance between random factor sequences even from incomplete information. The gray correlation degree is used to describe the importance of the factors, and the main influencing factors in the system were further extracted [43]. Thus, the grey relation entropy analysis was adopted herein to quantify the importance of the various factors on the low-temperature ductility of modified emulsified asphalt. The calculation steps are as following [44,45]:

a. Determine the reference sequence and comparison sequence.

$$\text{Reference sequence: } X_0 = \{X_0(k)|k = 1,2,\dots n\} \tag{1}$$

$$\text{Comparison sequence: } X_i = \{X_i(k)|k = 1,2,\dots n\}\ (i = 1,2,\dots n) \tag{2}$$

b. Normalization processing.

Generally, the data in each factor column is incomparable due to different dimensions, so it is necessary to normalize the data to dimensionless. In this research, the normalization methods used for data preprocessing were shown in Equation (3) and Equation (4):

$$\text{Reference sequence : } Y_0 = \{X_0(k)/\overline{X_0}\,|\,k = 1,2,\dots n\} \tag{3}$$

$$\text{Comparison sequence : } Y_i = \{X_i(k)/\overline{X_i}\,|\,k = 1,2,\dots n\}\ (i = 1,2,\dots n) \tag{4}$$

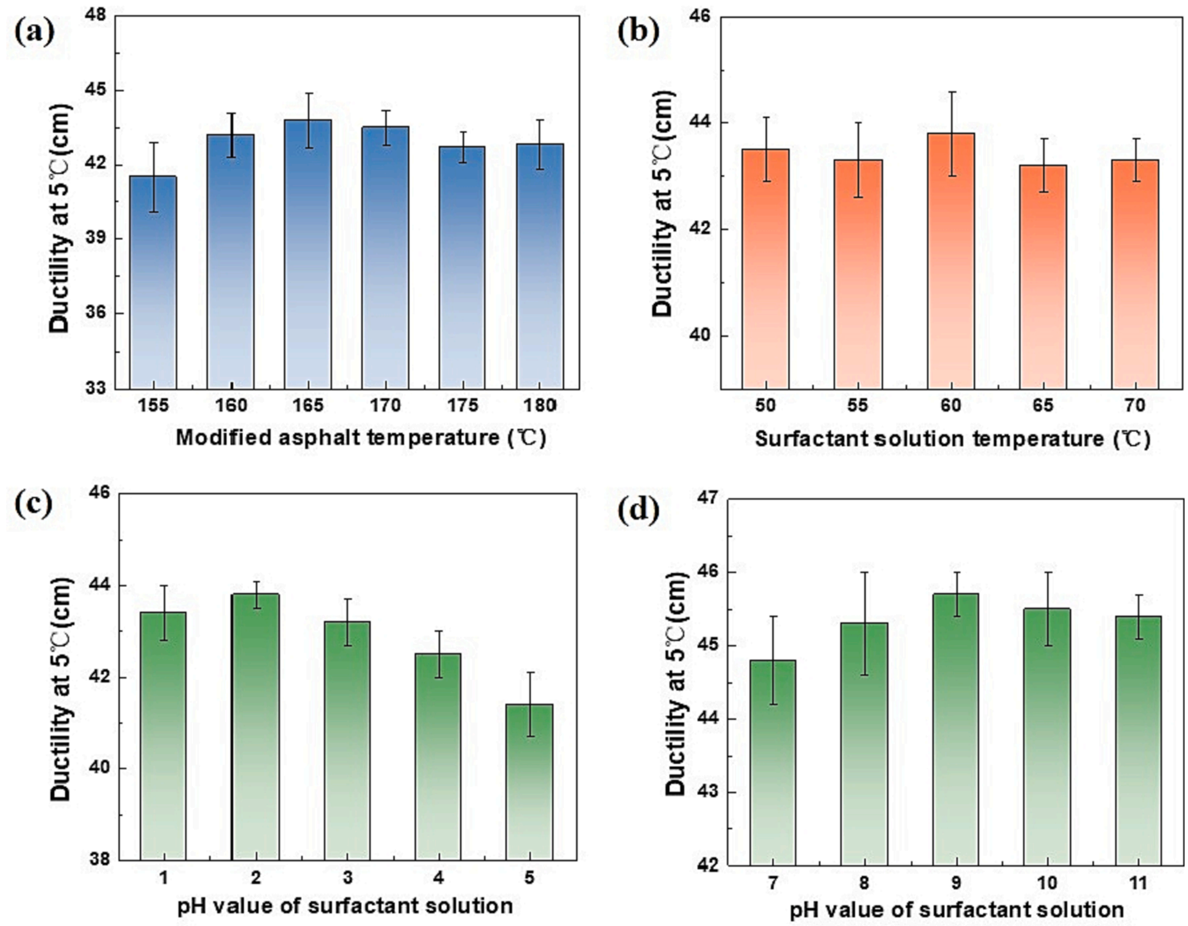

Fig. 5. The effect of (a) modified asphalt temperature (b) surfactant solution temperature on the ductility at 5 °C of PMC modified emulsified asphalt; The pH value of (c) PMC (d) SDBS surfactant solution on the ductility at 5 °C of modified emulsified asphalt.

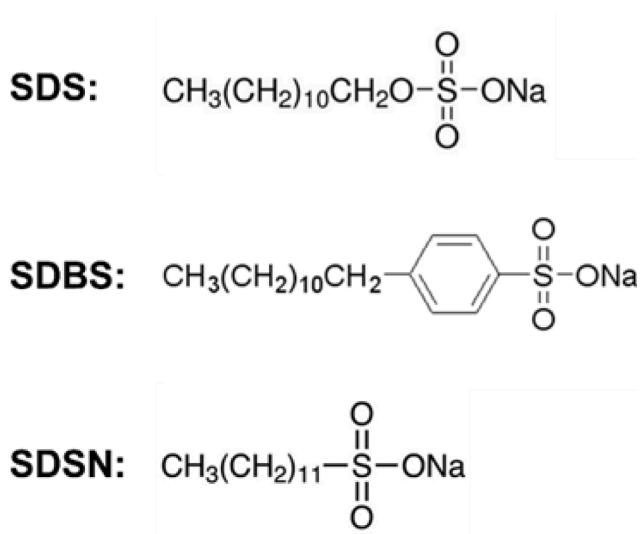

Fig. 6. The molecular formulas of SDS, SDBS and SDSN.

c. Calculate grey entropy relational coefficient.

According to the normalized sequences, the grey entropy relational coefficient is calculated to evaluate the relationship between the reference sequences and the comparative sequences. The grey entropy relational coefficient (ξ) is calculated by Equation (5):

Table 2
The grey relations between ductility at 5 °C and emulsifier structures.

Emulsifier	Ductility at 5 °C/cm	Molecular weight ratio of lipophilic group/hydrophilic group	C/H ratio	S/O ratio
SDS	36.5	1.76	0.48	0.25
SDBS	45.7	3.06	0.62	0.33
SDSN	38.4	2.11	0.48	0.33
Grey correlation grade	–	0.4892	0.8109	0.5508

Table 3
The grey relations between ductility at 5 °C and influencing factors.

No.	Ductility at 5 °C/cm	Emulsifier	Emulsifier content/wt%	Additive content/wt%
1	31.6	SDS	1.0	0.02
2	24.2	SDS	2.0	0.1
3	18.9	SDS	2.0	0.06
4	37.2	SDBS	1.0	0.1
5	33.3	SDBS	2.0	0.06
6	25.5	SDBS	3.0	0.02
7	30.7	SDSN	1.0	0.06
8	28.9	SDSN	2.0	0.02
9	17.6	SDSN	3.0	0.1
Grey correlation grade	–	0.8070	0.5828	0.5623

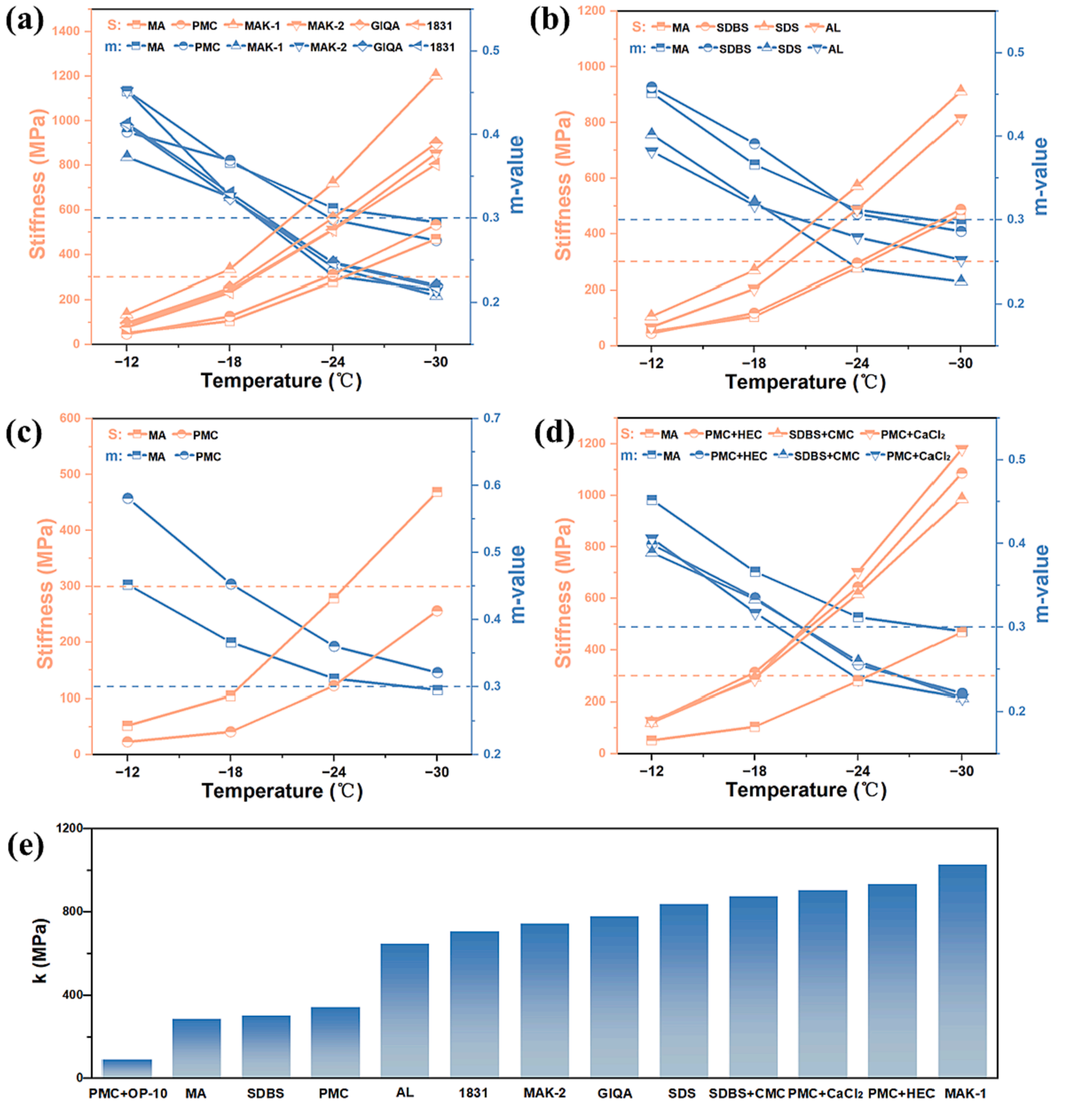

Fig. 7. The stiffness and m-values of (a) cationic emulsifiers (b) anionic emulsifiers (c) PMC/OP-10 (d) additives; (e) Comparison of k values of different modified emulsified asphalt at −18 °C (MA: modified asphalt).

$$\xi_i = \left| \frac{\min_{i=1,n}\min_{k=1,n}\Delta_i(k) + \rho\cdot\max_{i=1,n}\max_{k=1,n}\Delta_i(k)}{\Delta_i(k) + \rho\cdot\max_{i=1,n}\max_{k=1,n}\Delta_i(k)} \right| \quad (5)$$

where, ρ is the resolution coefficient (0.5 is generally used), $\Delta_i(k)=|Y_0(k)-Y_i(k)|$, $\min_{i=1,n}\min_{k=1,n}\Delta_i(k)$ and $\max_{i=1,n}\max_{k=1,n}\Delta_i(k)$ are the minimum difference and maximum difference, respectively.

Further, the grey relational grade (the average value of relational coefficient, γ_i) can be calculated by Equation (6).

$$r_i = \frac{1}{n}\Sigma\xi_i(k) \quad (6)$$

The higher grey relational grade indicates the stronger relevance between the reference sequence and the comparison sequence.

3. Results and discussion

3.1. Investigation on influencing factors of low-temperature ductility of modified emulsified asphalt

To unveil the relevance between microstructure and macroscopic low-temperature performance of modified emulsified asphalt, the influencing factors were firstly investigated (Figs. 4, 5).

In view of the poor compatibility between asphalt and water, emulsifiers are introduced to mix asphalt and water into a homogeneous liquid [46]. The ductility of modified emulsified asphalt was greatly affected by different types and contents of emulsifiers (Fig. 4a-c). When the emulsifier content was 1.5 wt%, the attenuation effect of the cationic emulsifier PMC, 1831, GIQA, MAK-2 and MAK-1 on the ductility of the

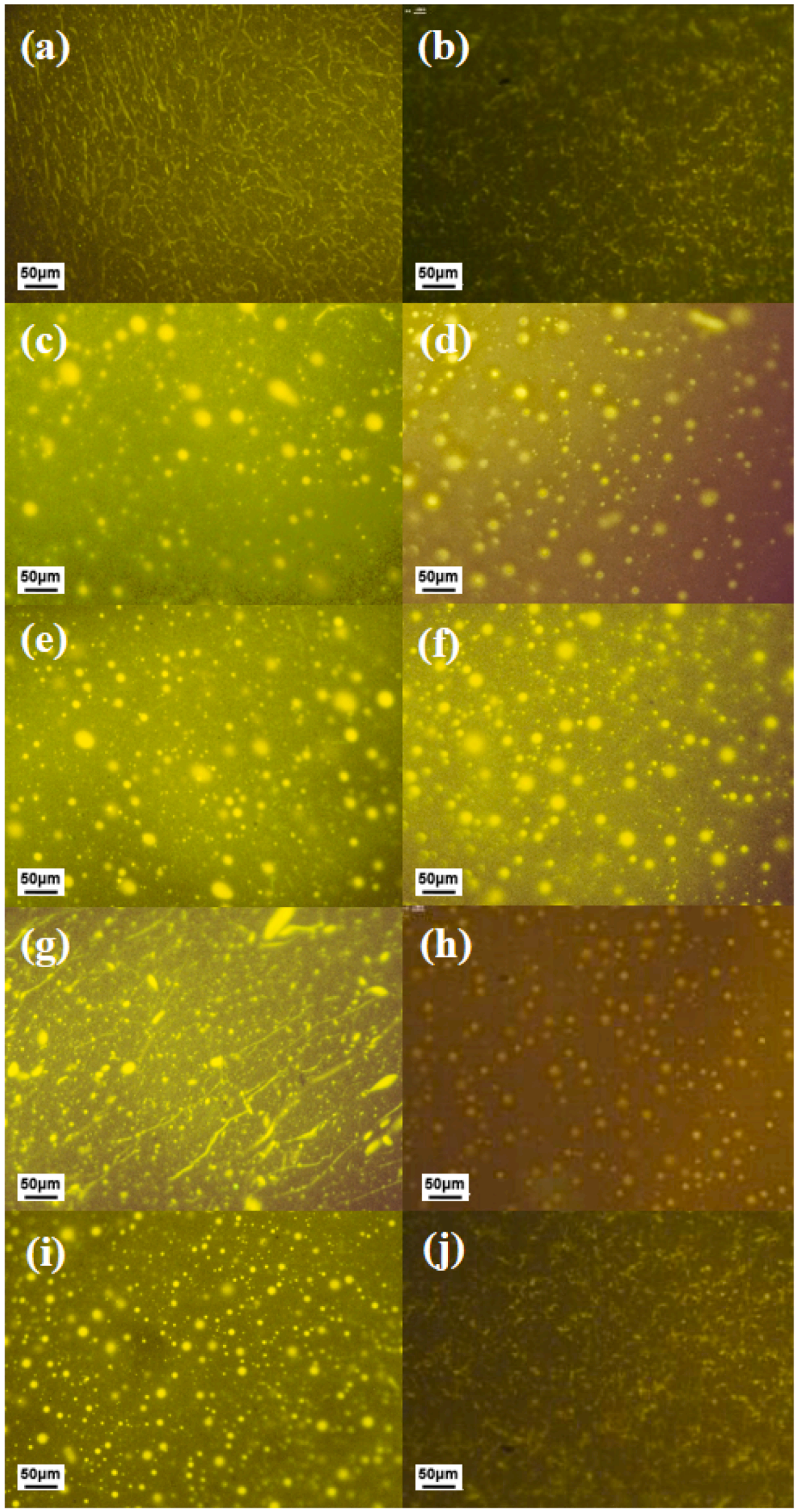

Fig. 8. FM of (a) modified asphalt (b) PMC (c) MAK-1 (d) MAK-2 (e) GIQA (f) 1831 (g) SDBS (h) SDS (i) AL (j) PMC + OP-10 modified emulsified asphalt.

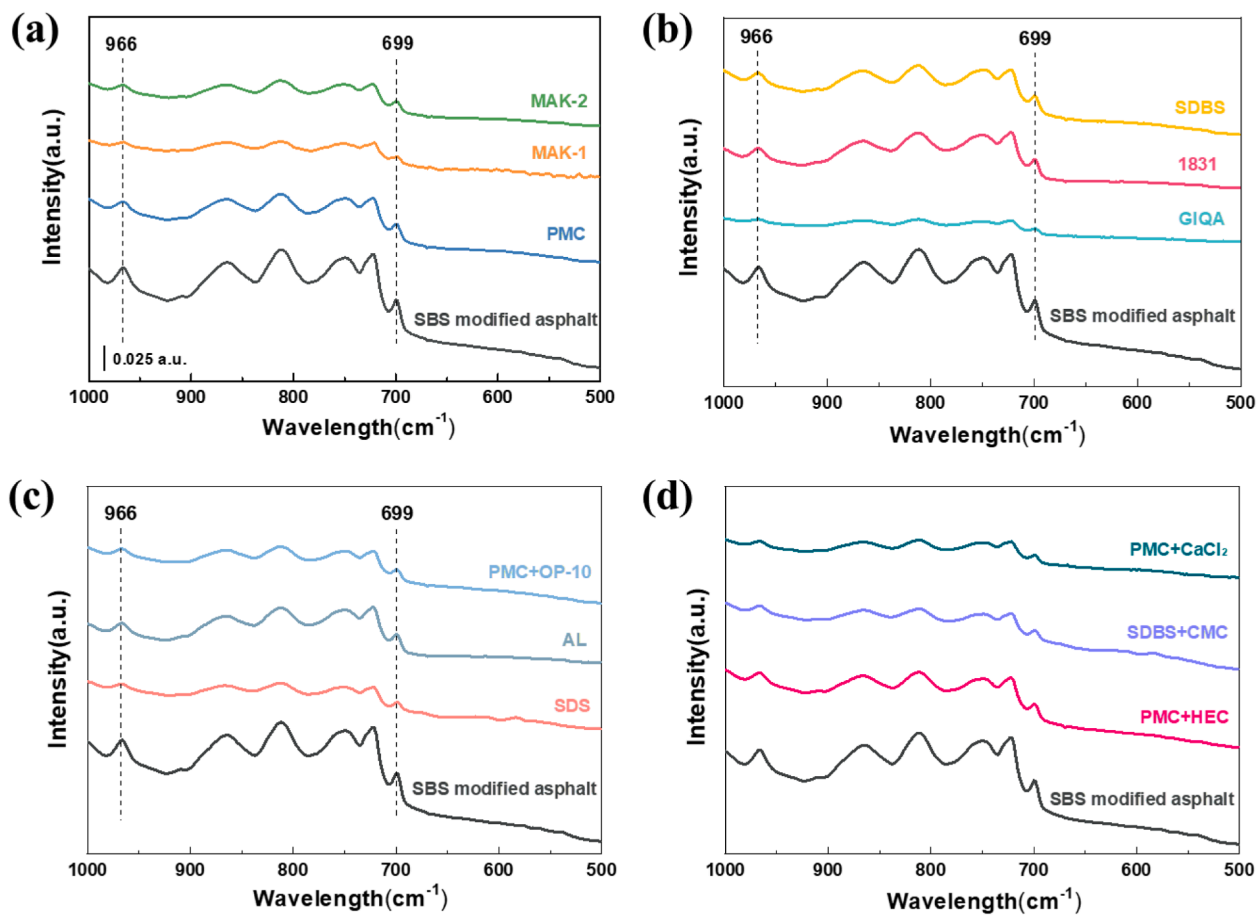

Fig. 9. FT-IR spectra of (a) PMC, MAK-1, MAK-2 (b) GIQA, 1831, SDBS (c) SDB, AL, PMC + OP-10 (d) PMC + HEC, SDBS + CMC, PMC + $CaCl_2$ modified emulsified asphalt before and after emulsification.

Table 4
Intensity ratios of absorption band of butadiene to styrene in modified asphalt and the evaporation residue of modified emulsified asphalt.

Material	Integral area at 966 cm^{-1}	Integral area at 699 cm^{-1}	Intensity ratio (R)
SBS modified asphalt	6.21	2.75	2.25
PMC	3.67	1.60	2.30
MAK-1	3.68	1.41	2.61
MAK-2	3.35	1.60	2.10
GIQA	2.37	1.12	2.12
1831	3.95	1.80	2.19
SDBS	3.21	1.45	2.22
SDS	3.26	1.37	2.38
AL	3.16	1.36	2.32
PMC + OP-10	4.81	2.16	2.23
PMC + HEC	5.38	2.20	2.44
SDBS + CMC	4.1	2.29	2.10
PMC + $CaCl_2$	3.00	1.22	2.46

modified emulsified asphalt was successively enhanced. The attenuation degree increased with the increasing of the emulsifier content. The results revealed that: although the fusion of the asphalt particles would not be hindered by the amine group on the PMC molecule, the ductility of the asphalt would also be reduced due to the impurities. MAK-1 and MAK-2 have the same hydrophilic imidazoline, while the lipophilic group of MAK-1 is lauryl and that of MAK-2 is cycloalkyl. The attenuation effect of the cycloalkyl group (MAK-2) on the ductility was less than that of the linear alkyl group (MAK-1), which was due to better structural similarity (cycloalkyl group) with asphalt. The hydrophilic groups of GIQA were composed of imidazoline heterocycles, hydroxyl groups, etc., which had large steric hindrance for demulsification, resulting in degradation of asphalt performance. In addition, due to the poor stability of 1831 in strong acid solution, the emulsification was incomplete and easy to demulsify. With the increasing of emulsifier content, the demulsification time was prolonged, and the asphalt performance would be attenuated.

As for anionic emulsifier, the attenuation effect of SDBS, AL, and SDS on the ductility of the modified emulsified asphalt was successively enhanced. The attenuation effect increased with the increase of the emulsifier content. Oxygen-containing functional groups (-SO_3, -SO_4) would lead to greater resistance during mixing and demulsification, resulting in difficult re-agglomeration of asphalt particles, difficult volatilization of water, and greater ductility loss. However, emulsifiers with phenyl group had good compatibility with asphalt (structural similarity), which was beneficial to maintain the low-temperature ductility.

Surprisingly, the ductility of the modified emulsified asphalt was increased by adding non-ionic emulsifier (OP-10). When molar ratio of PMC/OP-10 was 5, the ductility of modified emulsified asphalt evaporation residue became the best. Adding a certain content of OP-10 could improve the surface structure of emulsifier PMC on oil–water interface.

Furthermore, the effects of type and content of additives on low-temperature ductility were also thoroughly explored. Emulsion is a

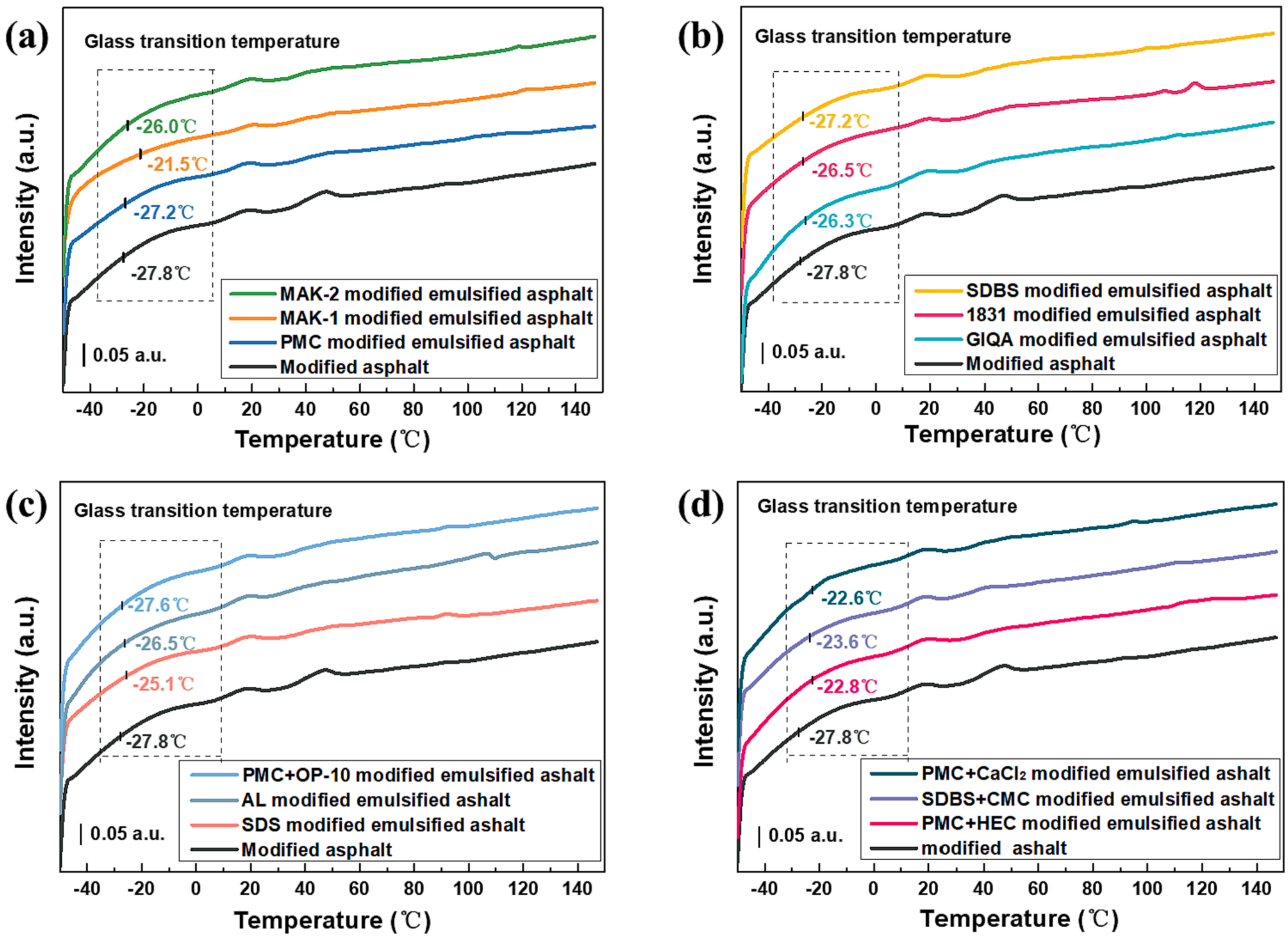

Fig. 10. DSC curves of (a) PMC, MAK-1, MAK-2 (b) GIQA, 1831, SDBS (c) SBS, AL, PMC + OP-10 (d) PMC + HEC, SDBS + CMC, PMC + $CaCl_2$ modified emulsified asphalt before and after emulsification.

Table 5
Tg of SBS modified asphalt before and after emulsification.

Material	Glass transition temperature/°C
SBS modified asphalt	−27.8
PMC	−27.2
MAK-1	−21.5
MAK-2	−26.0
GIQA	−26.3
1831	−26.5
SDBS	−27.2
SDS	−25.1
AL	−26.5
PMC + OP-10	−27.6
PMC + HEC	−22.8
SDBS + CMC	−23.6
PMC + $CaCl_2$	−22.6

thermodynamically unstable system [47]. A certain amount of additives would improve emulsification effect, enhance the stability of the emulsion, and reduce the cost of emulsified asphalt. Therefore, the effects of HEC, CMC, and $CaCl_2$ on the ductility of modified emulsified asphalt were investigated, and the results were exhibited in Fig. 4d. The ductility attenuation of organic additives (CMC, HEC) was greater than that of inorganic additives ($CaCl_2$). The ductility loss increased with the increasing of the additive content. The sodium carboxymethyl on CMC, the carboxyl groups and the hydroxyethyl groups on the HEC increased the water solubility, resulting that the asphalt particles were covered by thick hydration films. The re-agglomeration of asphalt particles during demulsification was hindered by the hydration film, resulting in ductility loss. The addition of $CaCl_2$ could enhance the electric double layer on asphalt emulsion particles, increase the repulsive force between the asphalt particles, which was not conducive to the ductility maintenance after demulsification.

In general, ductility at 5 °C was analyzed against the emulsifier content, molar ratio of PMC/OP and additive content (Fig. 4). Some hierarchy occurred between ductility and emulsifier content. A clear inflection point was underlined at a molar ratio (PMC/OP-10) of 3. The trends of the curves of ductility *vs.* additive content occurred similar with the same level of inflexion point around 0.02%. None significant difference occurred between anionic or cationic emulsifier, in term of ductility loss.

Apart from emulsifiers and additives, the emulsification process conditions are also vital to the low-temperature ductility of modified emulsified asphalt, such as the temperature of modified asphalt and surfactant solution, pH value of surfactant solution, etc. The effects of the temperature and pH value of the modified asphalt and surfactant solution (PMC, SDBS respectively) on the ductility were investigated.

The main purpose of tuning modified asphalt temperature was to control the viscosity [48]. Excessively high or low modified asphalt temperature would affect the emulsification effect of modified asphalt. When the temperature was too low, the viscosity of the asphalt was too high to flow, which increased the difficulty of asphalt emulsification. The effects of shearing and dispersing in the emulsification process were also poor. Increasing the modified asphalt temperature could effectively reduce the viscosity to a better fluidity, which was beneficial to improve the shearing and emulsifying effect. Fig. 5a showed that the modified asphalt temperature had little effect on the ductility due to the good

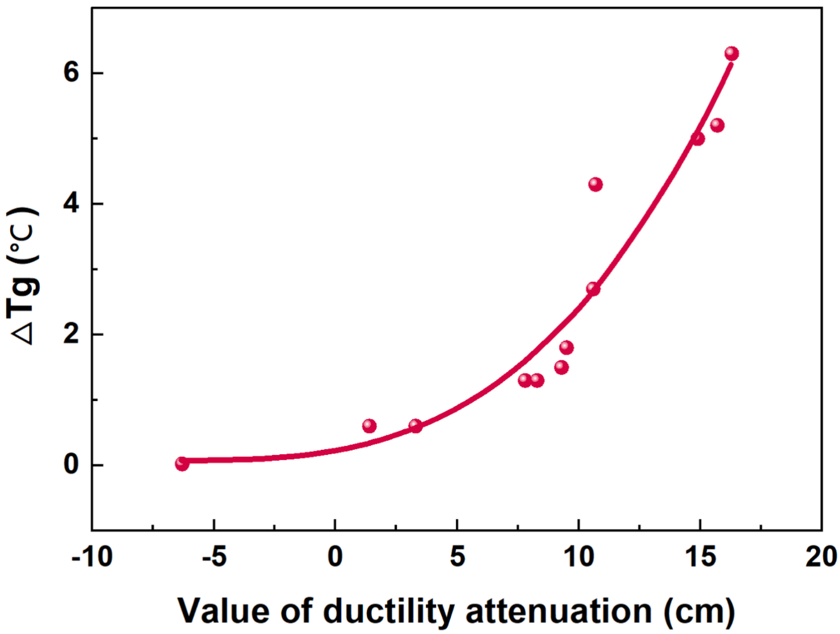

Fig. 11. The relevance between the change of Tg (ΔTg) and the value of ductility attenuation.

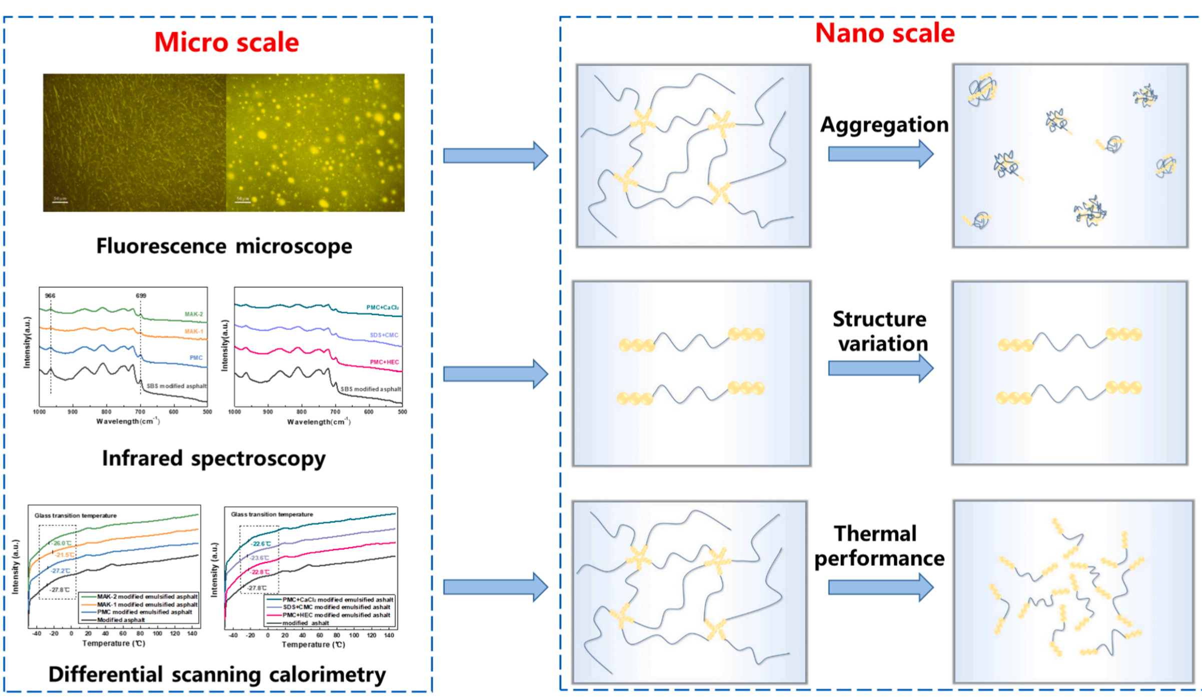

Fig. 12. Schematic illustration of the internal mechanism of ductility attenuation of SBS modified emulsified asphalt.

fluidity and emulsification between 155 °C and 180 °C.

Meanwhile, a certain temperature of surfactant solution is required to dissolve the emulsifier into water, increase the activity of the surfactant, and reduce the interfacial tension between water and asphalt. Hence, the effect of the surfactant solution temperature was also revealed, and the results were shown in Fig. 5b. The ductility of modified emulsified asphalt was arranged between 43.2 cm and 43.8 cm at different temperatures. Therefore, the temperature of surfactant solution had slight effect on the ductility of modified emulsified asphalt.

Additionally, the pH value can affect the ionization barrier on the surface of the emulsified asphalt suspension. Therefore, a suitable pH value of surfactant solution can improve the activity of the emulsifier and the stability of the emulsion. Generally, neutral or acidic surfactant solutions are suitable for cationic emulsifiers, while alkaline surfactant solutions are suitable for anionic emulsifiers. Thus, the effect of pH value of surfactant solution on the ductility was shown in Fig. 5c, d. The ductility of the PMC/SDBS modified emulsified asphalt increased firstly and then decreased with the increasing of pH value of the surfactant solution, which achieved a maximum with pH values of 2 and 9, respectively. When the pH value was between 1 and 3, the cationic emulsifier PMC was sufficient disassociated with H^+ in the surfactant solution. The active groups of the emulsifier could be protonated to show higher activity, resulting in the better performance of the obtained modified emulsified asphalt. When the pH value was higher than 3, the emulsifier activity decreased and the emulsification effect was poor. When the pH value was low, the high concentration of H^+ in the surfactant solution inhibited the ionization of anionic emulsifier SDBS. The decreasing of the active groups adsorbed on the interface led to poor emulsification effect. In contrary, the ionization of SDBS was promoted with increasing of the OH^- concentration at higher pH value. When the pH value was over 9, the negatively charged groups adsorbed on the interface became saturated, and the interface tension was reduced to a minimum, resulting in the optimal emulsification effect. Thus, the effect of the temperature change occurred less significant compared to the pH evolution of surfactant solution, and the optimal pH values were proposed: 2 for cationic and 9 for anionic.

To identify the contribution of the investigated factors, the grey relation entropy analysis was employed to quantify the relevance degree of the various factors on the low-temperature ductility of modified emulsified asphalt. The structure of emulsifier (lipophilic group/hydrophilic group) was greatly related to low-temperature ductility. SDS, SDBS and SDSN were selected as emulsifiers, and the molecular formulas were shown in Fig. 6. The emulsifier SDBS had the same hydrophilic group ($-SO_3$) as SDSN, but SDBS [$-Ph(CH_2)_{11}CH_3$] had phenyl subunits in lipophilic group. Therefore, the C/H ratios could be used to represent the structural differences of lipophilic groups between SDBS and SDSN. The high C/H ratio indicated that the emulsifier molecule had more unsaturated structures. The emulsifier SDS and SDSN had the same lipophilic group [$-(CH_2)_{11}CH_3$], while the hydrophilic group of SDS ($-OSO_3$) is larger than that of SDSN ($-SO_3$). Thus, the S/O ratios were used to describe the structural differences of lipophilic groups between SDS and SDSN. Therefore, the C/H ratio, S/O ratio and molecular weight ratio of lipophilic group/hydrophilic group were used to represent the structural differences of SDS, SDBS, and SDSN emulsifiers. The grey relations between ductility at 5 °C and emulsifier structures were shown in Table 2.

As shown in Table 2, the relevances between ductility at 5 °C and the emulsifier structure from strong to weak were as follow: C/H ratio, S/O ratio, and molecular weight ratio of lipophilic group/hydrophilic group. Emulsifiers with phenyl subunits had good compatibility with asphalt, which was beneficial to maintain the low-temperature ductility. The oxygen functional group would lead to the attenuation of the low-temperature ductility, which was mainly due to the large steric hindrance of the oxygen atom. In addition, the hydrogen-bonded water increased the fuse difficulty of the asphalt molecules, resulting in the attenuation of low-temperature ductility. The grey relation entropy analysis revealed that the C/H ratio of the emulsifier was the most important factor to affect the low-temperature ductility, which was consistent with the previous results.

According to above investigation, the influence of emulsification process conditions on low-temperature ductility was less than that of emulsifiers and additives. Therefore, the relevances of emulsifier type, emulsifier content and additive content with ductility at 5 °C were evaluated by grey relation entropy analysis. Based on the orthogonal experimental design method, three kinds of emulsifiers (SDS, SDBS, SDSN), three kinds of emulsifier contents (1.0 wt%, 2.0 wt%, 3.0 wt%), and three kinds of additive contents (0.02 wt%, 0.06 wt%, 1.0 wt%) were chosen for ductility test. Thus, the ductility at 5 °C was selected as the reference sequence, and emulsifier type, emulsifier content and additive contents were selected as the comparison sequences, the results of grey relation entropy analysis were presented in Table 3.

In Table 3, the order of the relevance's consequence was: emulsifier structure, emulsifier content, and additive content. Therefore, the C/H ratio of the emulsifier molecule is the main structural factor to correlate the low-temperature ductility of the emulsifier, which helps us to design the molecular structure of the emulsifier with sufficient low-temperature performance.

Moreover, the BBR test was used to verify the low temperature anti-cracking of asphalt. The stiffness (S-value) and relaxation rate (m-value) at −12, −18, −24 and −30 °C were obtained by BBR tests (Fig. 7a-d), which could estimate the low temperature anti-cracking of modified asphalt before and after emulsification. As the temperature decreased from −12 °C to −30 °C, the S-value increased while m-value decreased, indicating deteriorated low-temperature rheological behavior. The lower S-value and higher m-value indicated the inferior of low temperature anti-cracking of modified emulsified asphalt (except PMC + OP-10) than that of modified asphalt. With the decreasing of temperature, the low temperature anti-cracking of modified asphalt after emulsification was attenuated obviously. In Fig. 7 a-d, the variation ranges of S and m values were quite different, which was related to the structure of emulsifier. To further evaluate the low temperature anti-cracking of different types of modified emulsified asphalt, the k value (the ratio of S-value/m-value) at −18 °C was used for comparison (Fig. 7e). The k values of PMC and SDBS modified emulsified asphalt were similar to that of modified asphalt, indicating that the low temperature anti-cracking was less attenuated. The k value of PMC + OP-10 modified emulsified asphalt was lower than that of modified asphalt, indicating that the low temperature anti-cracking of modified asphalt was improved by introducing OP-10. The k values of MAK-1, MAK-2, GIQA, 1831, SDS, AL, SDBS + CMC, PMC + HEC, PMC + $CaCl_2$ modified emulsified asphalt were much higher than that of modified asphalt, indicating that the addition of these emulsifiers was unfavorable to low temperature anti-cracking. Therefore, the effect of the emulsifier on low-temperature cracking resistance obtained from the BBR test was similar with the data of ductility attenuation at 5 °C, which indicated that the combination of ductility test and BBR test could be an effective way to evaluate the low-temperature performance of asphalt.

3.2. The mechanism of influencing factors of evaporation residue ductility of SBS modified emulsified asphalt

To deepen the mechanism understanding of influencing factors of SBS modified emulsified asphalt, the FM was used to compare the distribution of SBS in asphalt before and after emulsification (Fig. 8). As shown in Fig. 8, yellow particles were precipitated and dispersed unevenly in the evaporation residue, which would be caused by the aggregation of uncross-linked SBS particles or uneven dispersion of the emulsifier. Therefore, the properties of asphalt changed after emulsification, which was macroscopically manifested as the ductility loss of the evaporation residue. Moreover, different emulsifiers had different effects on the two-phase morphology. The SBS structures of the PMC, PMC + OP-10, and SDBS modified emulsified asphalt had little change, which was consistent with their macroscopic performance (ductility). For MAK-1, MAK-2, GIQA, 1831, SDS, AL modified emulsified asphalt, the degrees of aggregation of SBS particles were greater, which macroscopically manifested the greater ductility loss.

Moreover, FT-IR was employed to investigate the microstructural change of modified asphalt before and after emulsification (Fig. 9). The FT-IR spectra of modified asphalt exhibit two characteristic absorption peaks at 699 cm^{-1} and 966 cm^{-1}, which ascribes to the stretching vibration of the subunit of polystyrene and polybutadiene of SBS, respectively. The structural change of SBS before and after emulsification in modified asphalt could be characterized by the intensity of these two characteristic absorption peaks. According to the Lambert-Beer law, the intensity of the two characteristic absorption peaks could be compared by integral area of the two peaks. Thus, the intensity ratios (R value) of the peaks at 966 cm^{-1} and 699 cm^{-1} in modified asphalt and evaporation residue were shown in Table 4. As aforementioned, the modified emulsified asphalt owned similar R value as modified asphalt, which indicated that the chemical structures of SBS were reserved in the asphalt after emulsification due to its high chemical stability.

On the basis of above investigations, DSC curves (Fig. 10) were employed to further reveal the Tg of SBS modified asphalt before and after emulsification (Table 5). When the temperature was less than 0 °C, the glass transition of the modified asphalt before and after emulsification occurred at −28 °C ~ −20 °C (slightly higher than that before emulsification), which was consistent with the ductility at 5 °C. After emulsification, the low-temperature cracking resistance of the modified asphalt became poor. Moreover, the Tg of PMC, PMC + OP-10, SDBS modified emulsified asphalt were increased smaller than that of modified asphalt, which was consistent with the ductility attenuation of these three modified emulsified asphalts. The Tg of MAK-1, MAK-2, GIQA, 1831, SDS, AL, SDBS + CMC, PMC + HEC, PMC + $CaCl_2$ modified emulsified asphalt had a larger increase compared with modified asphalt, which was consistent with the larger macroscopic ductility loss.

To further ensure the relevance between microstructural factors and macroscopic low-temperature performance, the change of Tg (ΔTg) was correlated with ductility attenuation (Fig. 11). The greater variation of Tg indicated greater ductility attenuation of modified emulsified asphalt. By fitting the relevance curve, the fitting equation between ΔTg and the value of ductility attenuation (X) was obtained, as shown in Equation 7. Thus, the ductility attenuation could be predicted through Tg results.

$$\Delta Tg = 0.0005X^3 + 0.01X^2 + 0.0668X + 0.2152 \tag{7}$$

Therefore, the schematic illustration of the internal mechanism of ductility attenuation of SBS modified emulsified asphalt was summarized in Fig. 12. The macro, micro and nano scales of modified asphalt were correlated, revealing in-depth that the aggregation and the inter-chains interaction of SBS were the internal mechanism leading to the ductility loss. The greater variation of the above-mentioned micro factors indicated the greater macro ductility attenuation, thereby giving feedback to guide industrial production.

4. Conclusion

Herein, the effects of emulsifier, additive, modified asphalt temperature, temperature and pH value of surfactant solution on the ductility of modified asphalt evaporation residue were investigated. Further, the influence mechanism of low-temperature ductility was analyzed from the microscopic point of view by FM, FT-IR and DSC characterization. The conclusions were as follows:

(1) Emulsifiers and additives had greater influence on the low-temperature ductility. Anionic and cationic emulsifiers had the similar emulsifying abilities depending on the comparable corresponding ductility. Adding a non-ionic emulsifier OP-10 could be a solution to improve the ductility of the modified asphalt. The grey relation entropy analysis revealed that the C/H ratio of the emulsifier was the most important factor to affect the low-temperature ductility.
(2) The influence of asphalt temperature on low-temperature ductility occurred to be limited. The effect of the temperature change occurred less significant compared to the pH evolution of surfactant solution. The optimal pH values were proposed: 2 for cationic and 9 for anionic.
(3) The effect of emulsifier on low temperature anti-cracking obtained from the BBR test was similar with ductility attenuation at 5 °C. The combination of ductility test and BBR test could be an effective way to evaluate the low-temperature performance of asphalt.
(4) The FM, FT-IR and DSC revealed that the aggregation and the inter-chains interaction of SBS were the internal reasons for the ductility attenuation. The change of Tg was proposed to correlate the microstructural factor with the ductility.

All in all, this research provides scientific guidance, feasible adjustment methods and effective solutions for the emulsification of modified asphalt.

CRediT authorship contribution statement

Yan Lin: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Chengduo Qian:** Resources, Validation, Writing – review & editing. **Jingtao Shi:** Resources, Validation. **Yuzhen Zhang:** Methodology, Resources. **Shisong Ren:** Resources, Writing – review & editing. **Guozhi Nan:** Methodology, Resources. **Xiangjun Kong:** Methodology, Validation, Investigation, Resources, Supervision. **Weiyu Fan:** Conceptualization, Resources, Visualization, Supervision, Project administration, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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