

## Research Article

# Evaluation of the Physical Performance and Working Mechanism of Asphalt Containing a Surfactant Warm Mix Additive

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This paper analyzes the influence of a surfactant warm mix additive on unmodified asphalt's conventional performance, viscosity-temperature characteristics, surface energy, and spreading performance on aggregate surfaces. The effect of the additive on asphalt's microstructure was explored by infrared (IR) spectral analysis. The results show the additive has little influence on the penetration, softening point, ductility, and viscosity-temperature characteristics of asphalt; this suggests that the additive does not work by lowering viscosity. The additive can reduce the zero-shear viscosity of asphalt, and adding too much can reduce antirutting performance. The additive also increases the asphalt's surface energy and the asphalt-water contact angle, while the polar component of surface energy decreases. The additive improves the spreading performance of asphalt on aggregate surfaces and reduces the asphalt-aggregate contact angle; the lower the temperature, the greater the reduction. IR spectral analysis shows that the additive does not react with asphalt—only physical blending occurs. The addition of a surfactant warm mix additive to asphalt allows asphalt mixtures to be more easily mixed and compacted at lower temperatures, thereby saving energy.

## 1. Introduction

Asphalt pavement has been widely used in road construction because it provides a smooth ride for vehicles and convenient maintenance; however, traditional hot mix asphalt (HMA) needs high temperatures to mix and compact, which consumes large amounts of energy and produces emissions, solid dusts, nitrogen oxides, and greenhouse gases [1, 2]. Such asphalt pavement engineering has high energy consumption and pollutant emissions, and so it does not satisfy China's commitments to energy conservation and emissions reduction. In recent years, warm mix asphalt (WMA) has been widely studied for its benefits of requiring less energy and being more environmentally friendly than HMA; its usage has grown rapidly [3]. WMA has similar performance

to HMA while requiring mixing and compaction temperatures that are 30–50°C lower than those used for HMA [4–6]. These reductions in mixing and compaction temperatures greatly reduce asphalt smoke emissions and energy consumption and can greatly reduce the aging of the asphalt binder, thus increasing the service life of asphalt pavement [7, 8]. As the compaction performance of low-temperature asphalt improves, asphalt's limited transportation and construction times can be extended [9]. In addition, the application of WMA to the recycling of waste asphalt mixtures can increase the proportion of reclaimed asphalt pavement (RAP) that can be reused [10]. At the same time, due to reduced production temperatures, asphalt mixing equipment experiences less wear, with potential economic benefits.

After decades of technological development, a variety of warm mix technologies have been developed, such as Sasobit organic additive warm mix technology, Aspha-min zeolite warm mix technology, Evotherm surfactant warm mix technology, and foamed asphalt warm mix technology [1, 11, 12]. These technologies have been effectively applied to the field of WMA [13]; however, the low-temperature asphalt-mixture compaction mechanism is not yet clear. In fact, researchers have noticed that the decrease in asphalt viscosity caused by a warm mix additive does not fully explain the decreased mixing and compaction temperatures required for on-site asphalt mixtures. On the contrary, the addition of warm mix additive can sometimes lead to increased asphalt viscosity [6, 14]. A surfactant warm mix additive does not change the viscosity of the asphalt binder [15], offering a different approach to the reduction of asphalt viscosity through synthetic waxes and foaming technology. However, research on the warm mix mechanism of this kind of additive and how the warm mix functions remains inadequate [16].

As the surfactant warm mix additive has little influence on the conventional specifications of asphalt, the compaction performance of asphalt mixtures is usually assessed to evaluate whether it has a warm mix effect or not; however, this method has a large margin of error and takes a long time. Knowing how to evaluate the warm mix effect based on asphalt properties is of great significance to road builders. The knowledge would help to establish product standards for warm mix asphalt. It would also allow the prediction of asphalt binder characteristics based on assessment at the oil refinery, helping to control the quality of asphalt products. According to some studies on the workability of WMA and HMA mixtures, the compactability of the mixtures does not increase linearly with the increase of temperature, but decreases once the mixture reaches a certain temperature [14, 17]. Previous studies have shown that this phenomenon may be related to friction and lubrication mechanisms in the contact zone between aggregates and to the thickness and lubrication characteristics of the asphalt film around the aggregate [18].

In recent years, the theory of asphalt surface tension and surface energy has been widely adopted in the study of asphalt mixture spreadability and adhesion [3–5]. According to surface tension theory, high-temperature asphalt produces the potential energy of internal contraction during the mixing and compaction of the asphalt and aggregate, that is, surface energy. When the asphalt contacts and adheres to the aggregate, a film will be formed. Due to surface tension, this film does not easily spread, which affects the adhesion of the asphalt and aggregate. However, a surfactant warm mix additive can change the surface tension and rheological parameters of asphalt, acting as a lubricant in the asphalt-aggregate contact area and improving the performance of asphalt-coating adhesion on aggregate surfaces. This effect increases the asphalt mixture's workability; however, due to a lack of effective characterization, research on this mechanism has been minimal.

This research aimed to study the warm mix mechanism of surfactant warm mix additives, using WMA prepared

using a common surfactant warm mix additive. The effects of the warm mix additive on the conventional physical properties, viscosity-temperature characteristics, and steady-state viscous flow properties of asphalt were investigated. Then, based on the theory of surface energy, the effects of the warm mix additive on the surface free energy of asphalt and the contact angle between the asphalt and aggregate were systematically studied. The effect of the warm mix additive on the microstructure of asphalt was studied by infrared (IR) spectral analysis, and the warm mix mechanism of the surfactant warm mix additive was discussed systematically.

## 2. Materials and Measurement

### 2.1. Materials

*2.1.1. Asphalt and Aggregates.* In this paper, asphalt with a penetration grade of 60 to 80 was used as the unmodified asphalt, provided by Qinhuangdao PetroChina Fuel Asphalt Co., Ltd.; its physical properties are shown in Table 1. The aggregate used in the experiment was the commonly used limestone; its properties are shown in Table 2.

*2.1.2. Warm Mix Additive.* The warm mix additive adopted in this experiment was an amide-type surfactant warm mix additive produced by Shanghai Longfu Materials Technology Co., Ltd. Its properties are shown in Table 3. Based on previous studies, when using 0.6 wt.% of warm mix additive (in unmodified asphalt) and when the voidage requirement is satisfied, the mixing and compaction temperature of the asphalt mixture can be reduced by 30°C [1].

*2.2. Preparation of Warm Mix Asphalt Samples.* Unmodified asphalt was heated to 135°C to allow it to flow well. Then, various amounts of warm mix additive were added and stirred at 400 rpm at a constant temperature of 135°C to obtain warm mix asphalt. Samples were prepared with warm mix additive amounts of 0.2 wt.%, 0.4 wt.%, 0.8 wt.%, and 1.0 wt.%.

*2.3. Conventional Performance Analysis of Warm Mix Asphalt.* According to the *Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering* (JTG E20-2011), the conventional performance of the warm mix additive was characterized. The Brookfield viscosity of the WMA was measured by a viscometer (Brookfield DV-II+) at a testing temperature range of 105–165°C and temperature interval of 10°C.

*2.4. Zero-Shear Viscosity Test.* Zero-shear viscosity is an indicator of the antirutting performance of asphalts [19]. It is usually determined by the Cross model according to the relationship between viscosity and the shear rate in the linear viscoelastic domain [20]. To measure the zero-shear viscosity of asphalt samples with different contents of warm mix additive, stress and strain scanning was carried out on

TABLE 1: Physical properties and chemical compositions of base asphalt.

Properties	Specifications	Measured values
Penetration (25°C, 0.1 mm)	T0604	70
Penetration index PI	T0604	-1.15
Softening point (R&B, °C)	T0606	48.6
Ductility (15°C, cm)	T0605	>100
Kinematic viscosity (135°C, Pa•s)	T0625	0.483
Density (15°C, g•cm <sup>-3</sup> )	T0603	1.029
Saturates/wt.%		20.46
Aromatics/wt.%		38.65
Resins/wt.%	SH/T 0509	27.56
Asphaltenes/wt.%		13.33

TABLE 2: The performance indices of the selected limestone aggregate.

Item	Test method	Test results
Crushed stone vale (%)	T0316	15.0
Los Angeles abrasion loss (%)	T0317	21.0
Flat and elongated particle content (%)	T0312	1.8
Less than 0.075 mm grain content (%)	T0303	0.3
Apparent relative density (g/cm <sup>3</sup> )	T 0304	2.72
Soft stone content (%)	T0320	0.5
Polished stone value (%)	T 0321	47

TABLE 3: Properties of warm mixing agent.

Item	Test method	Test results
Appearance	—	Brown viscous liquid
Density (20°C, g/cm <sup>3</sup> )	GB/T 6373	0.95
Viscosity (25°C, mPa•s)	GB/T 11409.8	931
Amine value (mgKOH/g)	GB/T 6365	560

each sample, and the linear viscoelastic range was obtained by a dynamic shear rheometer (DSR, anton-paar-mcr302) with a 25 mm plate diameter and spacing of 1 mm. Small-amplitude oscillation shear tests were then carried out on the samples to obtain isothermal scanning results in the viscoelastic range at frequencies of 0.1–50 rad/s and a temperature of 60°C. Finally, the Cross model was used to fit the zero-shear viscosities of asphalt samples with different amounts of warm mix additive.

**2.5. Measurement of Asphalt Surface Energy and Contact Angle.** The sessile drop method was used to measure the static contact angle of different liquids on the asphalt surface. The Owens–Wendt method was used to calculate the surface free energy of the asphalt and examine the influence of warm mix additive on the asphalt surface energy [21, 22].

Thomas Young introduced the concept of interfacial tension in a solid state system using the mechanical method. He derived a formula for the interfacial tension and contact angle of liquid-solid, gas-liquid, and gas-solid interfaces, called Young's equation [23, 24].

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL}, \quad (1)$$

where  $\gamma_L$  indicates the interfacial tension of a liquid-gas interface (that is, the liquid surface energy);  $\gamma_S$  indicates the interfacial tension of a solid-gas interface (that is, the solid surface energy);  $\gamma_{SL}$  indicates the interfacial tension of a solid-liquid interface; and  $\theta$  indicates the contact angle (the angle between  $\gamma_L$  and  $\gamma_{SL}$ ).

Later, Fowkes proposed the surface tension component approach. Fowkes, Van Oss, and others worked together to conclude that the sum of the dispersion and polar components of the intermolecular force can be regarded as surface energy. The surface energy calculation formula is shown in.

$$\gamma = \gamma^d + \gamma^p, \quad (2)$$

where  $\gamma$  indicates surface free energy (mJ•m<sup>-2</sup>);  $\gamma^d$  indicates the dispersion component of surface free energy (mJ•m<sup>-2</sup>); and  $\gamma^p$  indicates the polar component of surface free energy (mJ•m<sup>-2</sup>).

A liquid drop forms a fixed angle on a solid surface, and the resultant force of the three interfacial tensions of the gas, liquid, and solid phases is zero at any point of the three-phase boundary. The surface free energy of the interface is calculated as follows:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p}, \quad (3)$$

where  $\gamma_{SL}$  indicates the surface free energy of a solid-liquid interface ( $\text{mJ}\cdot\text{m}^{-2}$ );  $\gamma_S$  indicates the surface free energy of a solid ( $\text{mJ}\cdot\text{m}^{-2}$ );  $\gamma_L$  indicates the surface free energy of a liquid ( $\text{mJ}\cdot\text{m}^{-2}$ );  $\gamma_S^d$  indicates the dispersion component of solid surface free energy ( $\text{mJ}\cdot\text{m}^{-2}$ );  $\gamma_S^p$  indicates the polar component of solid surface free energy ( $\text{mJ}\cdot\text{m}^{-2}$ );  $\gamma_L^d$  indicates the dispersion component of liquid surface free energy ( $\text{mJ}\cdot\text{m}^{-2}$ ); and  $\gamma_L^p$  indicates the polar component of liquid surface free energy ( $\text{mJ}\cdot\text{m}^{-2}$ ).

Combined with Young's equation, it can be found that

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}. \quad (4)$$

Rearranging the above formula in the form of  $y = kx + b$ , it can be found that

$$\frac{\gamma_L (1 + \cos \theta)}{2} \frac{1}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d}. \quad (5)$$

To reduce experimental error, this study selected at least three different liquids to measure the contact angle. We plotted the coordinate with  $\gamma_L (1 + \cos \theta)/2 \times (\gamma_L^d)^{-0.5}$  as the vertical axis and  $(\gamma_L^p/\gamma_L^d)^{0.5}$  as the horizontal axis; then, the square of the intercept is the dispersion component and the square of the slope is the polar component.

It can be seen from formula (5) that the contact angle  $\theta$  must be measured to obtain the surface energy. In general, the contact angle is measured by the sessile drop method, which uses high-accuracy optical measurement; then, the surface free energy of the solid-liquid interface can be obtained [25]. This method has the following two basic requirements: (1) the surface of the sample should be smooth and even, and (2) the position of the solid surface should be changed many times to reduce experimental error. We used this method to measure the contact angles of liquid on asphalt surfaces and asphalt on aggregate surfaces.

**2.5.1. Asphalt Contact Angle Tests.** An optical contact angle measuring instrument (DSA-100, KRÜSS Scientific Instruments, Inc., Germany) was used to measure the static contact angle between warm mix asphalt surfaces and distilled water, glycerol and formamide [26]. The dispersion component, polar component, and surface energy of the three liquids are shown in Table 4. The surface energy of asphalt was calculated using Young's equation [25].

First, we heated the asphalt samples to  $165^\circ\text{C}$  and, once they were completely melted into liquid, we stirred them to mix evenly. Next, we immersed dry glass slides completely in hot asphalt. After the asphalt had fully adhered to a slide, it was slowly removed to obtain a smooth asphalt film on the

surface, as shown in Figure 1. After cooling, we trimmed around the slide. Finally, we titrated the three kinds of liquid on the asphalt film and measured the contact angles at room temperature ( $25^\circ\text{C}$ ). Three parallel tests were conducted on each sample and the average value was taken as the test result.

**2.5.2. Test of Asphalt-Aggregate Contact Angle.** The contact angle between the asphalt and aggregate was tested using the high-temperature module of the DSA-100 optical contact-angle measuring instrument. First, the aggregate was cut to create a flat surface. Next, coarse and then fine sandpaper were used to polish the surface of the aggregate. After polishing, the aggregate was cleaned with distilled water and dried to a constant weight in an oven at  $105^\circ\text{C}$ . The aggregate and asphalt were then placed in an oven and held at the test temperature for 30 minutes. Finally, we put the appropriate amount of asphalt into the high-temperature device of the contact-angle measuring instrument and placed aggregate in its temperature-preservation device. We then adjusted the instrument to make asphalt drop onto the surface of the aggregate. Measurements were taken once a second for a total of 10 s, and the process was then repeated two times; the average value was taken as the result. The measurement temperature range was  $60\text{--}140^\circ\text{C}$  with measurements taken at  $20^\circ\text{C}$  intervals.

**2.6. IR Spectral Analysis.** Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the functional groups of unmodified asphalt, warm mix additive, and warm mix asphalt; then, their chemical compositions were analyzed [27]. An infrared spectrometer (Thermo Science Nicolet IS 5) with a Thermo Science iD5 ZnSe ATR accessory was used in the tests. The scanning frequency was 32 times per minute and the wavenumber scan range was  $4000\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$ .

### 3. Results and Discussion

**3.1. Effect of the Surfactant Warm Mix Additive on Conventional Asphalt Performance.** To systematically study the working mechanism of the surfactant warm mix additive in the asphalt, we first investigated the effect of the amount of warm mix additive on the conventional physical properties of asphalt. The results are shown in Figure 2.

It can be seen from Figure 2 that the penetration grade and softening point of asphalt increased slightly after adding the warm mix additive. The maximum increase in penetration grade was 7.1% (at a warm mix additive content of 0.3 wt.%) and the maximum increase in the softening point was 1.6% (warm mix additive content = 0.8 wt.%). However, the ductility decreased slightly, with a maximum reduction of 15.1% (warm mix additive content = 0.4 wt.%). These analyses show that the warm mix additive has little effect on the conventional performance of asphalt.

In addition, the penetration index (PI) was used to investigate the effect of the warm mix additive on the temperature sensitivity of the asphalt. In penetration testing,

TABLE 4: Surface energy values and their components of three liquids.

Liquid type	Surface energy $\gamma_L$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	Dispersion component $\gamma_L^d$ ( $\text{mJ}\cdot\text{m}^{-2}$ )	Polar component $\gamma_L^p$ ( $\text{mJ}\cdot\text{m}^{-2}$ )
Distilled water	72.3	18.7	53.6
Glycerol	65.2	28.3	36.9
Formamide	59	39.4	19.6

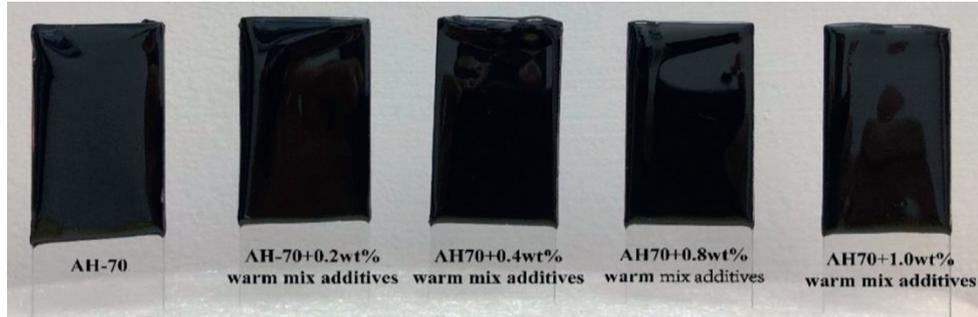


FIGURE 1: Warm mix asphalt binder samples and coated glass slides.

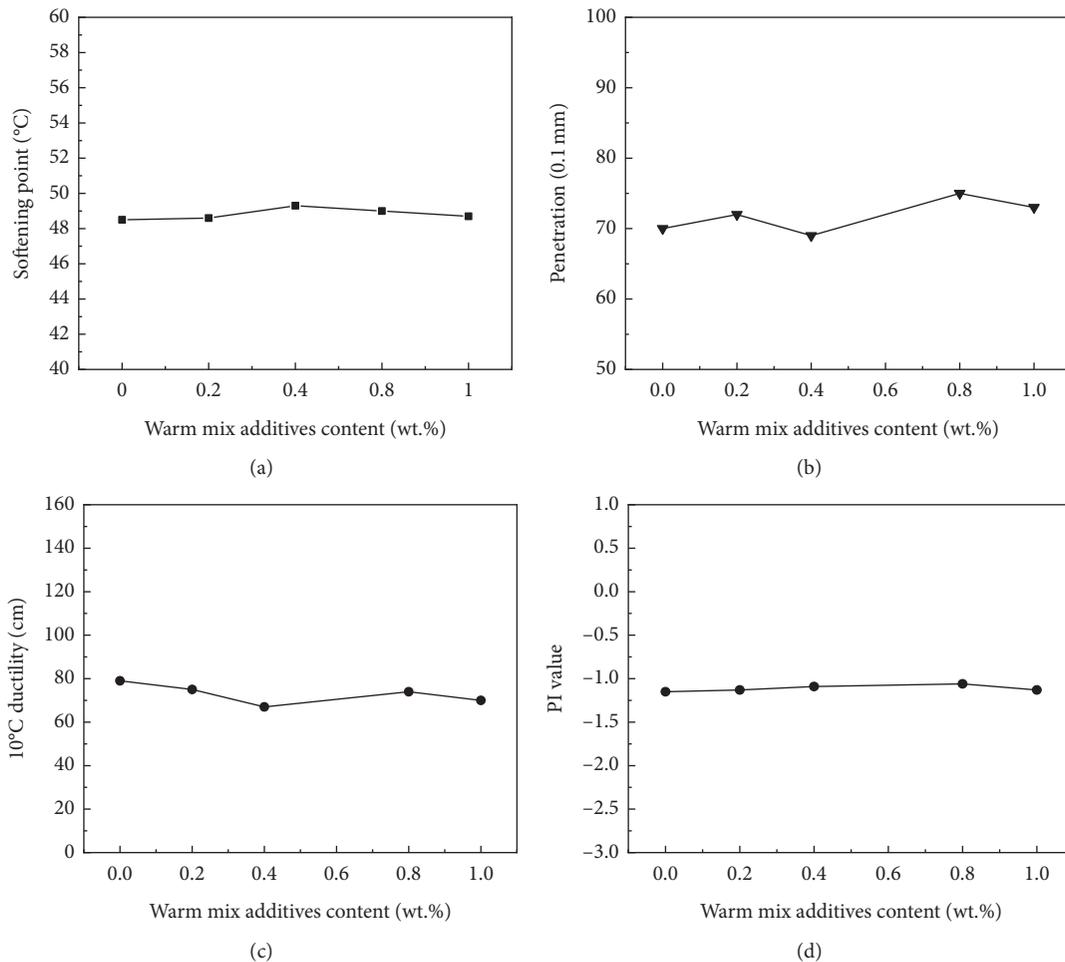


FIGURE 2: Effect of warm mixing additives on the performance of asphalt (a) softening point; (b) penetration; (c) 10°C ductility; (d) PI value.

when the penetration time and load are fixed, the logarithm of the penetration values measured at different temperatures is taken. Linear regression is then conducted according to the relationship between the penetration logarithm and temperature (formula (6)), meaning the PI can be calculated using the slope of the regression  $A$  in .

$$\lg P = AT + K, \quad (6)$$

$$PI = \frac{20 - 500A}{1 + 50A}, \quad (7)$$

where  $P$  indicates measured penetration (0.1 mm);  $T$  indicates measurement temperature ( $^{\circ}\text{C}$ );  $A$  indicates the slope of the regression line; and  $K$  indicates the intercept of the regression line on axis  $\lg P$ .

The higher the PI, the lower the temperature sensitivity of asphalt at medium temperatures. As shown in Figure 2(d), as the amount of warm mix additive increases, the asphalt PI increases slightly and the temperature sensitivity of the asphalt is improved. However, all the asphalt PI values are very close despite different additive amounts, which indicates that the warm mix additive has little influence on the asphalt's temperature sensitivity.

**3.2. Effect of Surfactant Warm Mix Additive on Asphalt Viscosity-Temperature Performance.** In this paper, a Brookfield rotary viscometer was used to test the viscosity of WMA at high temperatures ( $>60^{\circ}\text{C}$ ; Figure 3(a)). The slope of the viscosity-temperature curve was obtained using Walther and Saal's simplified formula, as recommended by ASTM 2493, to characterize the temperature sensitivity of asphalt at high temperatures (see Figure 3(b)). The calculation formula is shown in

$$\lg(\lg\eta) = n + m \cdot \lg T, \quad (8)$$

where  $m$  is the slope of the regression line;  $n$  indicates the intercept of the regression line on the  $\lg(\lg\eta)$  axis;  $\eta$  is viscosity (mPa·s); and  $T$  is temperature (K).

The absolute value of  $m$  is usually called the viscosity-temperature index (VTS) of asphalt; the smaller the VTS, the smaller the temperature sensitivity of asphalt materials at high temperatures. The results are shown in Table 5.

For a traditional hot mix asphalt mixture, the mixing and compaction temperature can be determined according to the viscosity-temperature curve, in which the viscosity suitable for mixing is  $0.17 \pm 0.02$  Pa·s and the viscosity suitable for compaction is  $0.28 \pm 0.03$  Pa·s [28]. As can be seen from Figure 3, the influence of the warm mix additive on the viscosity of asphalt is very small, and the higher the temperature, the smaller the differences in the asphalt viscosity-temperature curve when different amounts of warm mix additive are used. When the temperature exceeds  $125^{\circ}\text{C}$ , the viscosity-temperature curves of WMA with different amounts of additive are basically coincident. It also can be seen from Figure 3 that when the temperature is lower than  $125^{\circ}\text{C}$ , the viscosity of the WMA is higher than unmodified asphalt, except for the mix with 1.0 wt.% of additive. In addition, as the amount of warm mix additive increases, the

VTS of asphalt first increases and then decreases; however, the VTS values are approximately similar, which further indicates that the warm mix additive has little effect on the temperature sensitivity of asphalt at high temperatures.

The above analysis shows that the surfactant warm mix additive does not achieve the effect of warm mixing through a mechanism of reducing the viscosity of the asphalt binder.

**3.3. Effect of Surfactant Warm Mix Additive on Asphalt Zero-Shear Viscosity.** Zero-shear viscosity  $\eta_0$  is an indicator of the antirutting performance of asphalt [19]. It is an important performance indicator used to evaluate WMA. The relationship between the steady-state viscosity and shear rate of asphalt with different amounts of warm mix additive in the linear viscoelastic domain is shown in Figure 4.

It can be seen from Figure 4 that the viscosity of all samples decreases with an increase in shear rate, which indicates shear thinning. All flow curves can be fitted with the Cross model using formula (9) to determine the zero-shear viscosity.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{[1 + (\lambda \cdot \dot{\gamma})^d]}, \quad (9)$$

where  $\eta_0$ ,  $\eta_{\infty}$ ,  $\lambda$ ,  $\dot{\gamma}$ , and  $d$  indicate the zero-shear viscosity and the viscosities corresponding to the infinite shear rate, characteristic time, shear rate, and flow index, respectively. The viscosity curve-fitting parameters of asphalt with different amounts of warm mix additive are shown in Table 6. The zero-shear viscosity of asphalt decreases with an increase in the amount of warm mix additive; the decrease is obvious with warm mix additive amounts of 0.8 wt.% and 1.0 wt.%. This result shows that too much warm mix additive degrades the antirutting performance of asphalt; therefore, an appropriate amount should be determined when using this kind of warm mix additive.

**3.4. Effect of Warm Mix Additive on Asphalt Surface Energy.** The above analysis shows that the addition of a surfactant warm mix additive to asphalt does not significantly affect its high-temperature viscosity. However, research has shown that this kind of warm mix additive can improve the interface between the asphalt and aggregate so that friction at microinterfaces can be reduced [19, 27].

The contact angles between WMA containing different amounts of additive and three test liquids (water, formamide, and glycerol) were measured using the contact-angle measuring instrument (as shown in Figure 5). The data were validated using the method proposed by Kwork: for a given solid surface, there should be a linear relationship between  $\gamma_L$  and  $\gamma_L \cos\theta$  for the three kinds of liquids; otherwise, the test should be repeated. The contact angles of the three liquids on the surface of WMA, and the linear correlation coefficients ( $R^2$ ) between  $\gamma_L$  and  $\gamma_L \cos\theta$ , are shown in Table 7.

Table 7 shows that the dispersion coefficients of the contact angles of the three liquids on the surface of WMA were all less than 1%, indicating the test had good

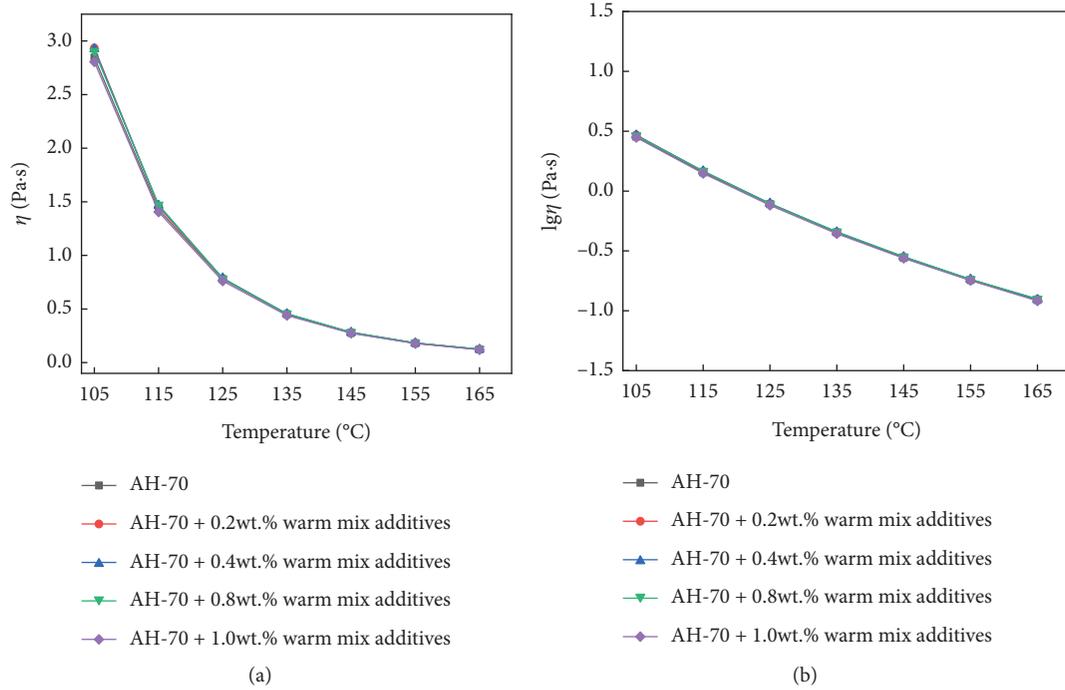


FIGURE 3: Effect of warm mixing additives on the viscosity-temperature performance of asphalt.

TABLE 5: Viscosity-temperature curve-fitting equation of warm mix asphalt.

Warm mix additives content (wt.%)	Viscosity-temperature curve equation	VTS	$R^2$
0	$y = -0.02264x + 2.76198$	0.02264	0.9899
0.2	$y = -0.02272x + 2.78014$	0.02272	0.9888
0.4	$y = -0.02278x + 2.78756$	0.02278	0.9897
0.8	$y = -0.02266x + 2.77364$	0.02266	0.9894
1.0	$y = -0.0226x + 2.75045$	0.0226	0.9896

repeatability. It can also be seen from Table 7 that the contact angle between the asphalt and water increased with the addition of the warm mix additive. This result indicates that the warm mix additive improves the hydrophobicity of asphalt.

In addition, according to Young's equation, when many kinds of liquids are used to test the surface energy of asphalt, we can plot  $y = \frac{(1 + \cos \theta)/2}{\sqrt{\gamma_l^p/\gamma_l^d}}$  for  $x = \sqrt{\gamma_l^p/\gamma_l^d}$  and use the linear fitting method to process a scatter diagram (see Figure 6). The square of the slope of the fitted curve is the polar component of the surface energy ( $\gamma_s^p$ ), and the square of the intercept is the dispersion component of the surface energy ( $\gamma_s^d$ ), the sum of which is the surface energy ( $\gamma_s$ ) [25]. The surface free energies of asphalt with different amounts of warm mix additive and the linear correlation coefficients of the fitted curves in Figure 6 are shown in Table 8.

It can be seen from Figure 6 that the linear correlation coefficients of the fitted curves ( $R^2$ ) are all greater than 0.99. The fitted curves reflect the relationship between the polar

and dispersion components of surface energy well, indicating that the measured contact angle data is highly valid. It can be seen from Table 8 that the polar component of asphalt decreases and the dispersion component increases with the addition of warm mix additive, as does the surface energy. The decrease in the polar component indicates that the capacity of asphalt to adsorb water molecules is weakened while the hydrophobicity of asphalt is enhanced, which is consistent with the change in the contact angle between the asphalt and water.

A possible reason for the increase in asphalt surface energy after adding warm mix additive is that the asphalt becomes easier to spread and forms a larger surface area. According to colloid theory, most asphalts are colloidal systems formed by asphaltene with high molecular weight and high aromaticity dispersed in a soluble medium with low molecular weight. Due to their tendency to self-aggregate, asphaltene molecules play an important role in the combination of asphalt and aggregate [29]. Previous studies have shown that a surfactant can increase the dispersibility

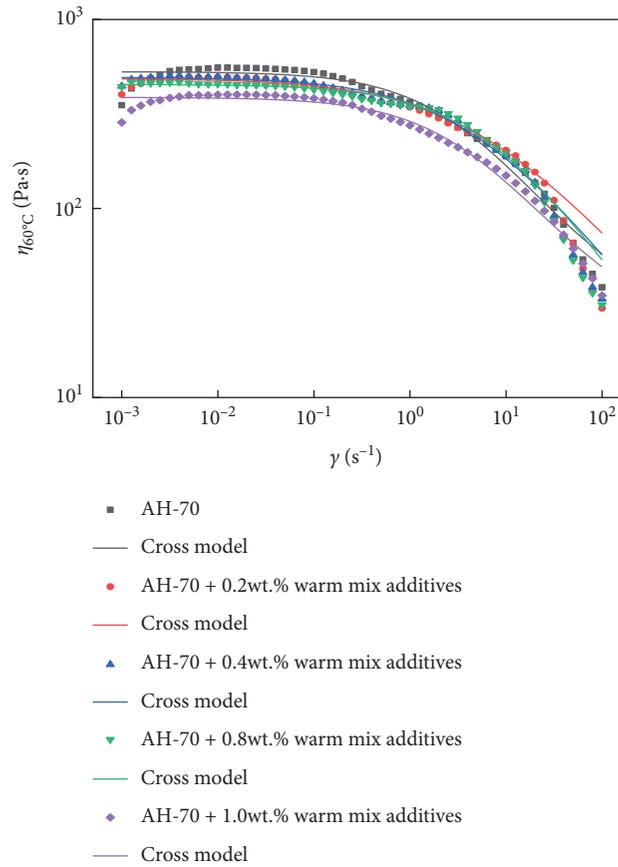


FIGURE 4: Flow curves of asphalt with warm mix additives content at 60°C.

TABLE 6: The fitting parameters of flow curves by Cross model.

Warm mix additives content (wt.%)	$\eta_0$ (Pa·s)	$\eta_{\infty}$ (Pa·s)	$\lambda$ (s)	$D$
0	501.95	27.26	0.33	0.79
0.2	487.86	$2.96 * E^{-49}$	0.19	0.60
0.4	494.66	$1.75 * E^{-122}$	0.23	0.66
0.8	453.88	$3.10 * E^{-133}$	0.16	0.73
1.0	364.84	22.58	0.27	0.77



FIGURE 5: Measurement of contact angle between liquid and asphalt.

TABLE 7: Contact angle between asphalt and liquid.

Warm mix additives content (wt.%)	Water		Glycerol		Formamide	
	Contact angle (°)	$C_V$ (%)*	Contact angle (°)	$C_V$ (%)	Contact angle (°)	$C_V$ (%)
0	99.79	0.68	96.01	0.65	91.84	0.53
0.2	100.80	0.52	96.08	0.46	91.90	0.29
0.4	102.30	0.71	96.11	0.72	92.06	0.69
0.8	102.80	0.84	96.54	0.29	92.00	0.71
1.0	103.20	0.26	96.64	0.52	92.08	0.69

\*  $C_V$ : coefficient of variation.

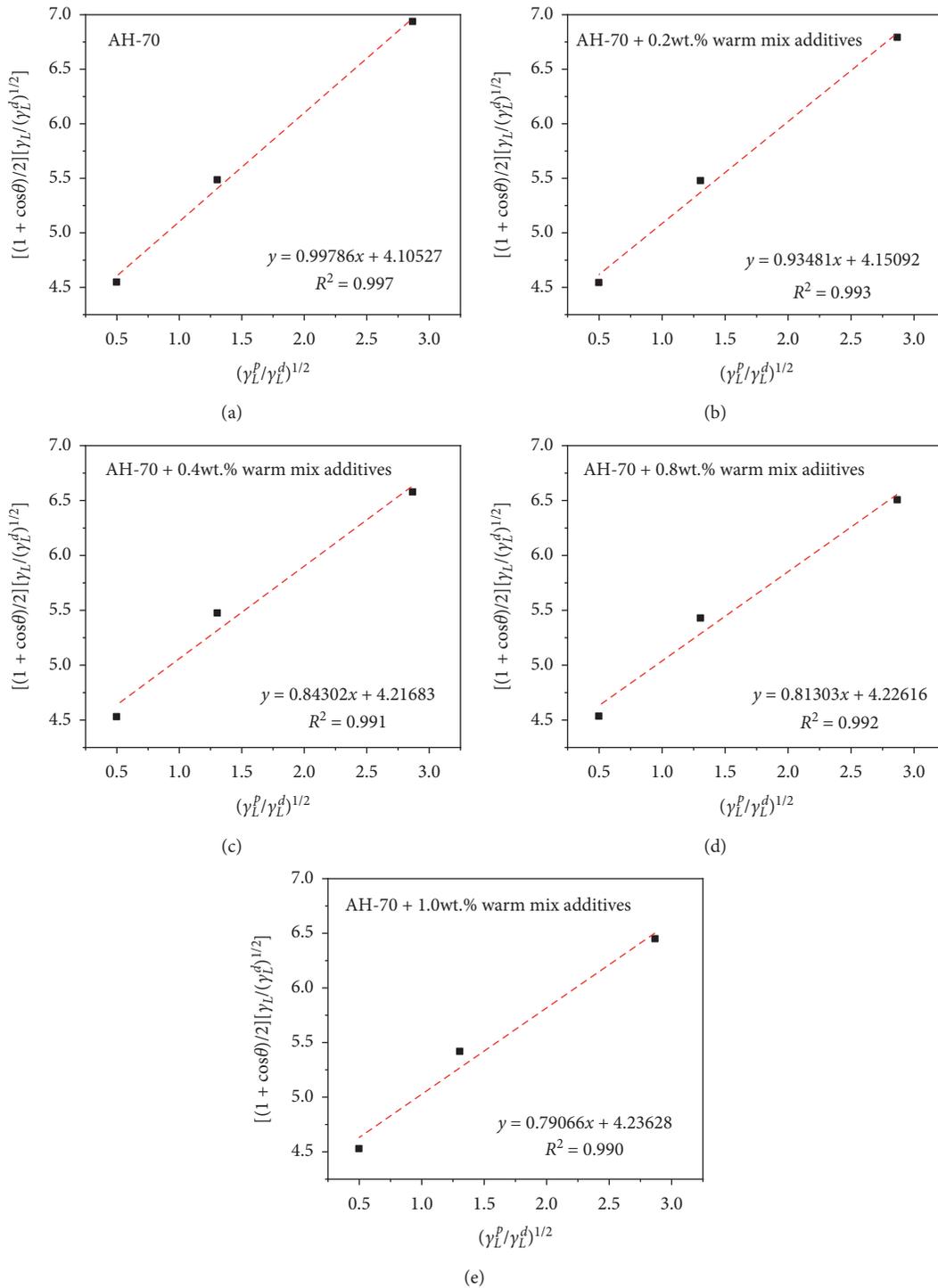


FIGURE 6: Fitting curve of surface energy component of asphalt sample.

TABLE 8: Surface energy and its component of asphalt sample.

Warm mix additives content (wt.%)	$\gamma$ (mJ·m <sup>-2</sup> )	$\gamma^p$ (mJ·m <sup>-2</sup> )	$\gamma^d$ (mJ·m <sup>-2</sup> )
0	17.849	0.996	16.853
0.2	18.104	0.874	17.230
0.4	18.493	0.711	17.782
0.8	18.521	0.661	17.860
1.0	18.571	0.625	17.946

of asphaltene [30], and the better the dispersion performance, the greater the surface energy of asphalt. Furthermore, with increases in asphaltene dispersion, the spreading performance of asphalt on aggregate surfaces increases.

### 3.5. Effect of Warm Mix Additive on the Asphalt Contact Angle.

To verify the effect of the warm mix additive on the asphalt's ability to spread on aggregate surfaces, the contact angle of asphalt on aggregate surfaces was measured at service temperatures using a contact-angle measuring instrument with a high-temperature device (KRÜSS). To characterize the influence of the warm mix additive on the rate of asphalt spread on aggregate surfaces, curves of asphalt-aggregate contact angles, at different temperatures over time, were constructed.

It can be seen from Figure 7 that temperature is the main factor affecting the contact angle of the asphalt on the aggregate surface. Under the same conditions, the higher the temperature, the smaller the contact angle, which indicates that the asphalt spreads more easily on aggregate surfaces with increasing temperatures. At all temperatures considered, the asphalt-aggregate contact angle decreases with an increasing amount of warm mix additive. At the same time, the lower the test temperature, the greater the decrease in contact angle and the more rapid its rate of change. At temperatures of 80°C and 100°C, when the content of warm mix additive was 0.8 wt.% and 1.0 wt.%, the asphalt-aggregate contact angles were greatly reduced. The higher the test temperature, the smaller the difference in contact angle between the asphalt and aggregate mixed with different amounts of warm mix additive. This result indicates that, with increases in temperature, the influence of the warm mix additive on asphalt spreading performance decreases. At temperatures of 120°C and 140°C, the asphalt-aggregate contact angles for each asphalt sample are very similar.

In practical engineering, the purpose of using WMA is to achieve mixing and compaction at relatively low temperatures (30–50°C lower than with HMA). However, lower temperatures cause higher viscosity and worsen fluidity, which hinders the spreading of asphalt on aggregate surfaces. The above research shows that the addition of a surfactant warm mix additive can improve this spreading performance. Furthermore, the lower the temperature, the greater the improvement, meaning a WMA asphalt with

warm mix additive can be well mixed and compacted at a low temperature, thus satisfying practical and workability requirements.

The above analysis shows that the surface energy of asphalt increases with the addition of a surfactant warm mix additive. The material has the characteristic of going from a high-energy state to a low-energy state, and the greater the surface energy is, the more unstable it is. Only by reducing the surface area can the surface energy be reduced [20]. Therefore, the greater the surface energy of asphalt, the stronger its adsorption capacity and the more easily it can spread on aggregate surfaces. Especially at relatively low temperatures, a warm mix additive can improve the aggregate-spreading performance of asphalt, which makes it easy to mix and compact at lower temperatures. The above analyses describe the working mechanism of a surfactant warm mix additive.

### 3.6. Effect of Warm Mix Additive on the Microstructure of Asphalt.

One of the most commonly used methods for identifying the molecular structure of organic compounds is IR spectral analysis. The chemical bonds or functional groups of different molecular structures are represented by the size and position of absorption peaks in IR spectra. To explore whether there is a chemical reaction between the surfactant warm mix additive and unmodified asphalt that might affect the asphalt performance and warm mixing effect, we analyzed the IR spectra of unmodified asphalt, the warm mix additive, and WMA (Figure 8). Comparison reveals whether the wave peak, intensity, and functional groups in WMA are different to those of unmodified asphalt.

As shown in Figure 8 and Table 9, the characteristic IR absorbance peaks of unmodified asphalt are distributed in the range of 3000–700 cm<sup>-1</sup> and are mainly concentrated within 1700–700 cm<sup>-1</sup>, where there are 12 obvious peaks. The characteristic IR absorbance peaks of warm mix additive are distributed in the range of 3400–700 cm<sup>-1</sup>, including 14 obvious peaks. The characteristic absorbance peaks of warm mix additive and unmodified asphalt are obviously different, except for the peaks at 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup>. The IR spectrum of WMA includes all the peaks of unmodified asphalt and some strong absorbance peaks of warm mix additive. Due to the small amount of warm mix additive, the relatively weak peaks of warm mix asphalt are not evident in the WMA spectrum; however, there are no

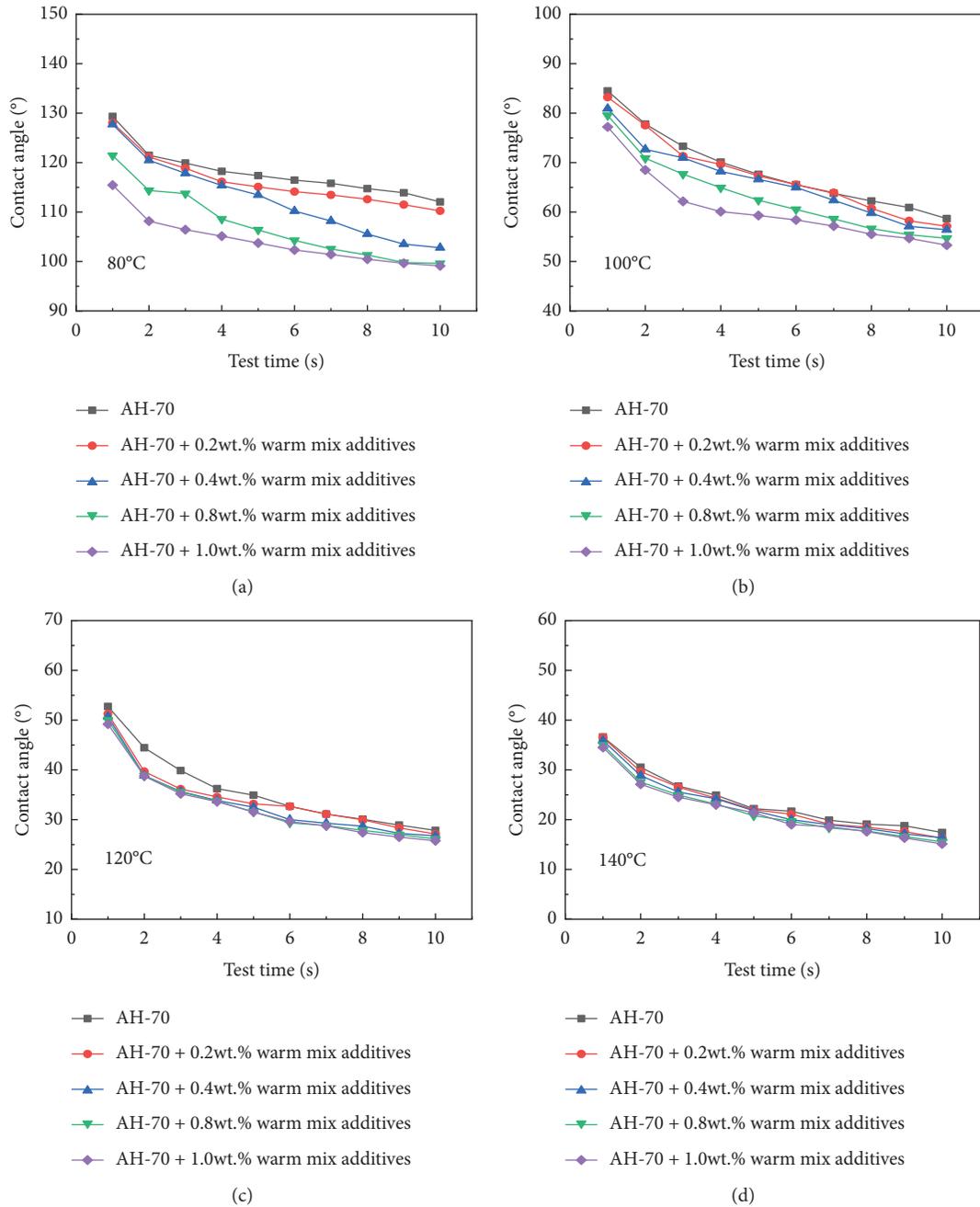


FIGURE 7: Contact angular diffusion curve of asphalt sample and aggregate at different temperatures.

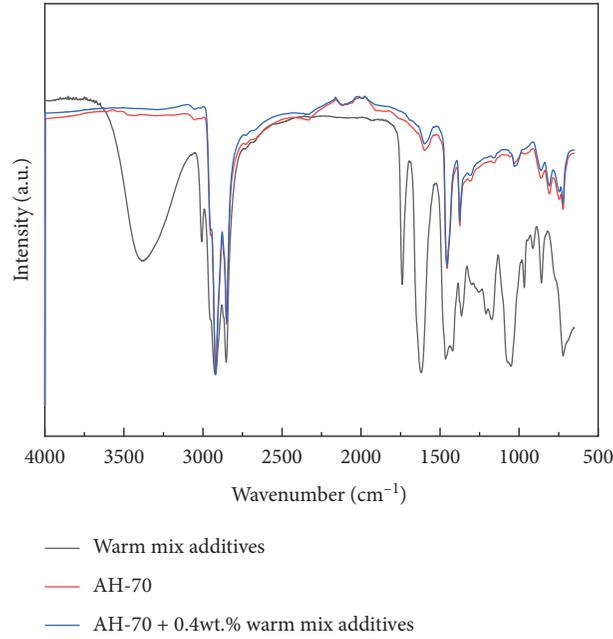


FIGURE 8: IR spectra of warm mix additives, AH-70 asphalt, and warm mix asphalt.

TABLE 9: IR characteristic absorption peaks of base asphalt, warm mix additives, and warm mix asphalt.

IR absorption peaks (cm)	Warm mix additives	Base asphalt	Warm mix asphalt
3383 <sup>-1</sup>	●		
3007 <sup>-1</sup>	●		
2920 <sup>-1</sup>	●	●	●
2850 <sup>-1</sup>	●	●	●
1739 <sup>-1</sup>	●		
1620 <sup>-1</sup>	●		
1600 <sup>-1</sup>		●	●
1465 <sup>-1</sup>	●		
1450 <sup>-1</sup>		●	●
1420 <sup>-1</sup>	●		
1380 <sup>-1</sup>		●	●
1364 <sup>-1</sup>	●		
1300 <sup>-1</sup>		●	●
1210 <sup>-1</sup>	●		
1173 <sup>-1</sup>	●		
1050 <sup>-1</sup>	●		
1030 <sup>-1</sup>		●	●
966 <sup>-1</sup>	●	●	●
913 <sup>-1</sup>	●		
900 <sup>-1</sup>		●	●
858 <sup>-1</sup>	●		
810 <sup>-1</sup>		●	●
720 <sup>-1</sup>	●	●	●

new peaks except for those of unmodified asphalt and warm mix additive. This result indicates only physical blending between the unmodified asphalt and warm mix additive, with no chemical reactions occurring. In other words, the working mechanism of the surfactant warm mix additive is through changes to physical friction rather than a chemical reaction.

#### 4. Conclusions

Based on surface energy theory and via analysis of conventional performance, viscosity-temperature performance, steady-state rheological properties, surface energy, and the spreadability of asphalt on aggregate surfaces, the working mechanism of surfactant warm mix additive was

investigated and its effect on the asphalt microstructure analyzed. The following conclusions can be drawn:

- (1) The effect of the warm mix additive on the conventional performance of asphalt was investigated. With an increasing amount of additive, the penetration grade and softening point of asphalt increase slightly, while ductility decreases slightly. The additive has little effect on the conventional performance of asphalt.
- (2) The effects of the warm mix additive on the viscosity-temperature characteristics and zero-shear viscosity of asphalt were studied. The additive has little effect on asphalt viscosity. The higher the temperature, the smaller the differences between the viscosity-temperature curves of asphalt containing different amounts of additive. The warm mixing effect of the additive was not obtained by reducing the viscosity of the asphalt binder. In addition, the additive reduces the zero-shear viscosity of asphalt. A high content of additive reduces the rutting performance of asphalt.
- (3) The effect of the warm mix additive on asphalt surface energy was studied. The additive increases the contact angle between the asphalt and water, decreases the polar component of surface energy while increasing the dispersion component, and increases the surface energy. The increases in asphalt-water contact angle and the polarity component indicate that the water-damage resistance of asphalt is enhanced.
- (4) The effect of the warm mix additive on asphalt spreadability on aggregate surfaces was studied. Temperature is the main factor affecting the contact angle of asphalt on aggregate surfaces. Under the same conditions, the higher the temperature, the lower the contact angle. At the same temperature, the warm mix additive reduces the asphalt-aggregate contact angle, and the lower the temperature, the greater the reduction and rate of change in contact angle with time. Therefore, the warm mix additive can improve asphalt spreadability on aggregate surfaces more than other additives, making asphalt easier to mix and compact at lower temperatures; thus, the warm mix additive is effective.
- (5) The effect of the warm mix additive on the microstructure of asphalt was studied. The additive does not react with asphalt to form new substances but rather forms warm mix asphalt through physical blending.
- (6) According to our results, the working mechanism of asphalt containing a surfactant warm mix additive has now been described. The additive has little effect on the performance of the base asphalt and there are no chemical reactions with it. Hence, the additive does not work by reducing viscosity or through chemical reactions. The additive can improve the intermolecular lubrication of asphalt, making it

spread more easily on the aggregate and facilitating warm mixing.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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