

## Research Article

# Effects of Dioctyl Phthalate on Performance of Asphalt Sealant

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Dioctyl phthalate (DOP) was introduced into asphalt-based sealant as a plasticizer in this work. Four kinds of sealants with different DOP content were prepared, and thermal stability and low-temperature performance of five samples with asphalt as a control group were evaluated by fluidity test, softening point test, thermogravimetric-differential thermal analysis (TG-DTA), low-temperature tensile test, and differential scanning calorimeter (DSC), respectively. Furthermore, the mechanism of DOP on sealant properties was analyzed by Fourier transform infrared spectroscopy (FTIR) and fluorescence microscope. Results show that DOP can significantly improve the low-temperature performance of sealant, but slightly deteriorate the high-temperature performance. This is because DOP can supplement the light component of sealant and enhance the fluidity of the internal components. On the one hand, DOP reduces the apparent activation energy of sealant and lowers the barrier to chemical reactions, indicating that DOP is slightly detrimental to the thermal stability of sealant. On the other hand, DOP greatly reduces the glass transition temperature of sealant and improves its low-temperature performance. However, there is no evident chemical reaction between DOP and sealant, and physical effects play a major role in the effects of DOP on sealant properties. In addition, DOP can promote the expansion and cross-linking of the polymer in the sealant and ultimately enhance the compatibility between asphalt and polymer molecules. In short, DOP is recommended as a plasticizer to prepare asphalt sealants with excellent properties.

## 1. Introduction

Defects such as cracks, ruts, potholes, and subsidence are prone to occur during the period of pavement service. Among them, cracks, as the most important pavement disease, should be paid more attention [1–4]. Cracks can not only affect the appearance of the pavement but also have a great impact on the performance of the pavement if not treated in time [5]. The effects of the bearing capacity of cars on the pavement can cause cracks to expand gradually and develop into serious pavement diseases such as potholes [6]. In addition, rainwater can invade the subgrade through the cracks, which can reduce the mechanical strength and stability of the subgrade, and greatly increase the repair cost in the later stage [7, 8].

The common treatment method for pavement cracks is grouting [9] or caulking technology [10]. Cracks that are more sensitive to temperature and environment should be repaired and maintained by grouting technology. The required sealant should have good adhesion to the crack wall so that it will not fall off when the crack shrinks or expands. While caulking technology should be used for the cracks that are not sensitive to temperature and environment. The construction process of caulking technology is simpler compared with grouting technology, but the repairing effect is not as good as that of grouting technology.

Sealant can be mainly divided into three types: high-temperature heating type, normal temperature type and resin type [11]. The high-temperature heating type sealant is mainly based on modified asphalt or rubber asphalt; normal temperature type sealant is mainly based on emulsified

asphalt or modified emulsified asphalt; and resin sealant is mainly based on polysulfide resin or silicone resin. The high-temperature heating type sealant is suitable for large-scale promotion due to its excellent performance and relatively low cost [12]. Many researchers have improved the performance of the high-temperature sealant by adding different modifiers to the original asphalt. For example, Li [13] determined the best preparation process of the asphalt-based sealant containing styrene-butadiene-styrene block copolymer (SBS), plasticizer, and rubber powder through orthogonal experiments. Zhang et al. [14] prepared a new type of asphalt-based sealant with three modifiers of SBS, polyurethane, and silicone. Li et al. [15] reviewed the mechanism, performance, and application of polyurethane sealant. Tan et al. [16] improved the repeatable repair ability of asphalt-based crack sealant by adding two kinds of microcapsules. In addition, solvent deasphalted has also been used to prepare asphalt-based sealants [17].

Plasticizers including dioctyl phthalate (DOP) have a wide range of applications in asphalt materials. Fan et al. [18] compared the effects of plasticizers on the mechanical properties of sealant suitable for permeable pavement. Wang [19] studied effects of red oil plasticizer on the performance of SBS modified asphalt, and results showed that plasticizer was unfavorable for the low-temperature performance of the modified asphalt. Wang et al. [20] used pavement crack stickers as a means of repairing pavement cracks and explored the influence of plasticizers on the performance of crack stickers. Cheng et al. [21] added DOP to the modified asphalt to improve the low-temperature performance degradation caused by the incorporation of linear low-density polyethylene (LLDPE). Zhang et al. [22] developed an asphalt mixture suitable for cold regions by adding DOP. Fu et al. [23] added dioctyl maleate and DOP as plasticizers to improve the flexibility of the mixture. In summary, there are few studies on the effects of DOP on the performance of sealant. In particular, the effect of DOP on the properties of complex polymer-containing sealant is still unclear.

In this work, asphalt sealant containing multiple polymers was prepared with asphalt, SBS, rubber powder, rubber oil, LLDPE, and stabilizers as raw materials, and effects of DOP content on the performances of sealant were also studied. The research results of this work are of positive significance for revealing the mechanism of DOP on the performance of sealant and preparing asphalt sealants with excellent properties.

## 2. Raw Materials and Test Methods

**2.1. Raw Materials.** The main raw materials of the sealant prepared in this work include asphalt, rubber powder, LLDPE, SBS, and DOP, and their properties are shown in Tables 1–5, respectively. In addition, all sealant samples in this work were blended with the same content of stabilizers to improve the compatibility between asphalt and modifiers. Properties of asphalt were tested according to Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering in China (JTG E20-2011) [25].

**2.2. Preparation of Asphalt Sealant.** In this work, four kinds of asphalt sealant with different DOP content (0%, 1%, 3%, and 5%) were prepared with other main raw material contents being set as 5% SBS, 15% CR, 5% rubber oil, 2% LLDPE, and 0.4% stabilizer. And asphalt was set as a control group to compare and analyze properties of asphalt sealant.

The main preparation steps of the asphalt sealant in this work are as follows: (1) put asphalt into a 165°C oven to a flowing state, and then transfer it to the heating device of a high-speed shear and keep the same temperature; (2) turn on the shear and start shearing with an initial shear rate of 2000 r/min; (3) blend rubber extender oil into asphalt during shearing and raise the temperature of the mixture of asphalt and rubber extender oil to 180°C; (4) increase the shear rate to 4000 r/min; (5) add SBS, rubber powder, LLDPE particles, and DOP in sequence and shear for 1.5 h; (6) add stabilizer after adjusting the shear rate to 2500 r/min; (7, 8) adjust the temperature to 175°C, continue shearing and maintain for 1 h, and then stop; (9) put the mixture into an oven at 60°C to develop for 2 hours and finally an asphalt sealant sample is prepared. Figure 1 shows the flowchart of the preparation process of asphalt sealant.

### 2.3. Test Methods

**2.3.1. Softening Point and Fluidity Tests.** The high-temperature properties of sealant are characterized by softening point and fluidity tests together, and the softening point test was carried out based on Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering in China (JTG E20-2011) [25]. Although softening point test can measure the high-temperature performance of asphalt to some extent, the consistency between softening point and high-temperature performance is poor for sealant, so the high-temperature performance of sealant was further verified using the fluidity test.

The fluidity test refers to the rubber asphalt sealant and filler of pavement (JT/T 740-2009) [26]. The main test steps are (1) align the brass mold frame with the lower tinned plate and brush glycerin talc on the inner side of the mold frame to prevent adhesion; (2) heat the sample in an oven until it is completely flowing, then pour it into the brass mold frame to fill up; (3) shovel off the excess sample on the surface and keep the sample flat and then remove the brass mold frame after cooling for 2 h to form three specimens with uniform shapes and sizes; (4) move the tinned plate on a 75° tripod to an oven and heat the sample at 60°C for 5 h; and (5) take the average value of the flows of the three samples as the flow result of this sample.

**2.3.2. Thermal Stability Test.** In order to further analyze the high-temperature performance of samples, thermogravimetric-differential thermal analysis (TG-DTA) was adopted in this work to analyze the thermal stability of asphalt as well as the sealant with different DOP dosage. The main test steps are (1) take an aluminum crucible and put it on the thermal balance of the instrument, close the side cover of the instrument, and stabilize the mass of the crucible for 10 s, then

TABLE 1: Properties of asphalt.

Properties	Results	Specification [24]	Test methods
Penetration (25°C, 5 s, 100 g; 0.1 mm)	81	80–100	T0604-2011
Softening point (°C)	45	≥44	T0606-2011
60°C dynamic viscosity (Pa·s)	147	≥140	T0620-2011
Ductility (10°C, 5 cm/min, cm)	36	≥30	T0605-2011
Wax content (distillation method, %)	1.1	≤2.2	T0615-2011
Flash point (°C)	260	≥245	T0611-2011
Solubility (%)	99.7	≥99.5	T0607-2011
Residue after RTFOT	Mass loss (%)	−0.02	≤±0.8
	Penetration ratio (25°C, %)	61	≥57
	Ductility (10°C, 5 cm/min, cm)	9	≥8

TABLE 2: Properties of rubber powder.

Items	Relative density	Moisture content (%)	Metal content (%)	Sieve residue (%)
Test results	1.13	0.495	0.04	4.38

TABLE 3: Properties of LLDPE.

Items	Density (g/cm <sup>3</sup> )	Temperature at peak melting (°C)
Test results	0.918	121

TABLE 4: Properties of SBS.

Modifier	Structure	Block ratio (S/B)	Elongation at break (%)	Melt flow rate (g/10 min)	Tensile strength (MPa)
SBS	Linear	35/65	80.0	0.8	16

TABLE 5: Properties of DOP.

Appearance	Ester content (%)	Acidity (g/cm <sup>3</sup> )	Volume resistivity (m)	Flash point (°C)	Color (APHA)
Colorless transparent liquid	99.3	0.012	0.2	193	28

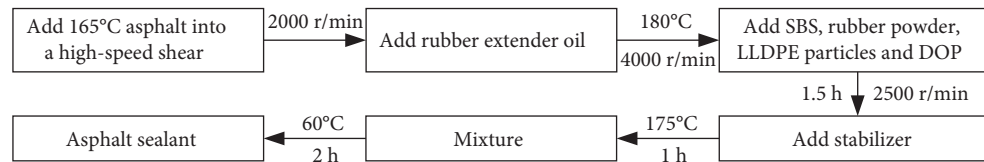


FIGURE 1: Flowchart of asphalt sealant preparation.

tare it and remove the crucible; (2) take 7 mg of sealant and put it into the crucible, move the crucible to thermal balance again, and close the side cover; and (3) set the temperature rise rate (four rates of 5 K/min, 10 K/min, 15 K/min, and 20 K/min were set in this work) and start the test and collect data. The influence of external weight changes should be strictly avoided on the instrument during the test to prevent the measured data from deviating. Three parallel tests were carried out for each group to reduce the measurement error.

**2.3.3. Low-Temperature Tensile Test.** The low-temperature tensile test was carried out in accordance with a self-designed fixture with reference to the Standard for Pavement Rubber Asphalt Grouting Adhesive (JT/T 740-2009) [26] to quantitatively characterize the low-temperature performance of the samples, as shown in Figure 2.

In this work, a microcomputer-controlled universal testing machine was used for testing the low-temperature tensile lengths of the samples. The main steps of the low-

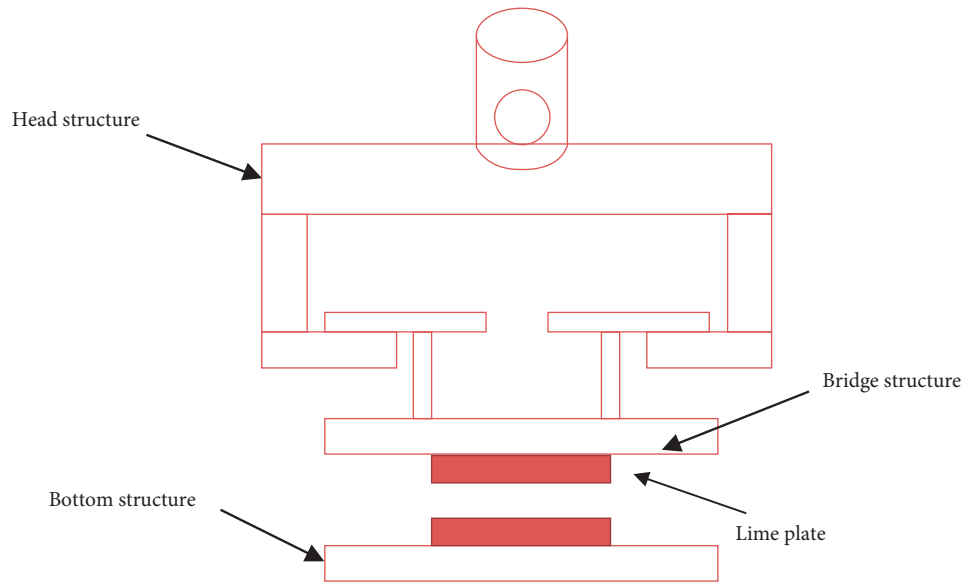


FIGURE 2: Self-designed fixture for low-temperature tensile test.

temperature tensile test are (1) heat the prepared sample in an oven to a flowing state and pour the sample into the 50 mm × 35 mm × 10 mm gap enclosed by the lime plate and the fixture; (2) disassemble the head structure and metal module of the fixture after the poured sample was cooled at room temperature for 2 h, and make the sample, the fixture bridging interface and the bottom structure lie flat on the horizontal table; (3) place the fixture bridge interface and bottom structure flat in a  $-20^{\circ}\text{C}$  low-temperature chamber for 2 h; (4) fix the fixture head structure and the upper structure of the universal testing machine, fix the fixture bottom structure and the bottom disc of the universal testing machine with strong glue in low-temperature environment, and quickly connect the fixture head structure and bridge structure; and (5) start the low-temperature tensile test with the 100 mm/min tensile rate [27] in a low-temperature environment; a complete tensile test is defined as the beginning of the tensile to the occurrence of brittle fracture. Three parallel tests were carried out for each sample, and the average value of the three measurements is defined as the final low-temperature test result of the sample.

The improved stretch fixture possesses the following advantages: (1) low cost, the self-made stretch fixture can be used repeatedly for many times, and the overall cost is low; (2) simple operation, the improved low-temperature stretch fixture has a simple structure, which greatly reduces the operation difficulty; (3) high testing efficiency, the experimental steps matched with the self-made stretch fixture are more simplified, mainly reflected in the cooling setting and stretching rate.

**2.3.4. Differential Scanning Calorimetry Test.** Sealant can be suffered from four states in turn when heated, which is glassy state, glassy-rubbery state, rubbery state, and fluid state, respectively, [28]. The glass transition temperature ( $T_g$ )

refers to the instantaneous temperature when the material changes from glassy state to high elastic state, which can reflect the low-temperature performance of the material to a certain extent [29]. In this work, the  $T_g$  of the sealant with different DOP dosage was tested using a differential scanning calorimeter (DSC) to quantitatively evaluate their low-temperature properties. The samples were tested under nitrogen atmosphere with a heating rate of  $10^{\circ}\text{C}/\text{min}$  and a temperature range from  $-60$  to  $40^{\circ}\text{C}$ . Three parallel tests were carried out for each group, and the average value was adopted as the testing result.

**2.3.5. Fourier Transform Infrared Spectroscopy Test.** The composition of sealant is complex with a variety of modifiers and additives, so Fourier transform infrared spectroscopy (FTIR) is applied to analyze the reactions and characteristics of the physicochemical changes between individual substances, and to analyze the modification mechanism of the modifiers and additives in depth from a microscopic perspective. In this work, the infrared spectra of asphalt and the sealant with different DOP dosage were collected by a Bruker Tensor II FTIR. The test was performed in a total reflection mode with 10 scans and a wave number range of  $400\text{--}4000\text{ cm}^{-1}$ . The temperature for the test was  $20^{\circ}\text{C}$ .

**2.3.6. Fluorescence Microscopy Analysis.** The microscopic characteristics of asphalt and the sealant with different DOP dosage were analyzed by a FluoroLog-3 fluorescence microscope under 400 times magnification based on the property that polymer can emit fluorescence under ultraviolet irradiation. The main steps are (1) dip an appropriate amount of sample in a fully flowing state with a glass rod and place it on the glass slide and make it self-level; (2) put the prepared sample under the objective of the fluorescence microscope, turn on the light source and color filter, and select the appropriate objective and eyepiece magnification

to observe the sample after the fluorescence microscope emits fluorescence; (3) adjust the slide position during the observation process until find the suitable position to observe the microscopic morphology of the sample and take pictures to obtain clear images.

### 3. Effects of DOP on Asphalt Sealant Properties

#### 3.1. High-Temperature Performance

**3.1.1. Softening Point and Fluidity.** In Figure 3, the softening point of sealant decreases and the flow increases with the increase of DOP dosage, indicating that DOP has a negative effect on the high-temperature performance of sealant. This is mainly due to the fact that DOP can supplement the light components inside the asphalt when DOP was fully mixed with asphalt under the action of high-speed shear and high temperature, so that the aromatic and saturated fractions in the asphalt increase and the percentage of recombination fraction decreases, which enhances the fluidity of the asphalt. It should be noted that the reduction in softening point of sealants with high DOP content is not significant. The softening point of the sealant with 5% DOP is only 5.23% lower than that of the sealant without DOP, but it is still much higher than that of asphalt.

**3.1.2. Thermal Stability.** In order to study the thermal stability of the sealant, the thermal behavior of the five samples at four heating rates of 5 K/min, 10 K/min, 15 K/min, and 20 K/min were investigated using a simultaneous thermal analyzer. Figure 4 shows the TG-DTG curves of the five samples at 10 K/min heating rate.

In Figure 4, the weight loss of the five samples can be mainly divided into two stages: the temperature of the first stage is from 300°C to 500°C and the temperature of the second stage is from 500°C to 800°C. The first stage is the main mass loss stage of the sample, which can be due to the volatilization of light components such as saturated hydrocarbons and aromatic hydrocarbons in asphalt and the decomposition of polymer macromolecules and heavy asphalt components. In the second stage, the loss mass of sample continues as the temperature increases due to the further volatilization of recombinant components in asphalt and carbonization of polymer residues, but the amount of mass loss is much less than that in the first stage.

The three main thermal stability indexes of asphalt and the sealant without DOP are shown in Table 6. In Table 6, the  $T_p$  of the sealant without DOP is larger than that of the asphalt, indicating that sealant possesses a better thermal stability. Since the sealant contains SBS, SBS can absorb light components such as saturated hydrocarbons and aromatic hydrocarbons in asphalt. This can make the light components less volatile and decomposes during the first stage of mass loss, thereby improving their thermal stability. The quality loss at  $T_p$  of the sealant without DOP is more than that of the asphalt, which is mainly due to the addition of several modifiers, the asphalt components, and modifiers volatilize together during the first stage. The remaining mass of the sealant without DOP is much larger than that of the

asphalt, which can be also mainly contributed to the addition of several modifiers to the sealant. Polymer residues account for a large proportion in addition to the carbonization of the heavy components in the asphalt after two stages of quality loss.

The influence of DOP content on the three main indicators of the thermal stability of the sealant is shown in Figure 5. In Figures 5(a) and 5(b), the  $T_p$  of the sealant gradually decreases and the quality loss at  $T_p$  gradually increases with the increase of the DOP content. This is mainly because the molecular weight of DOP is 390.55, which belongs to the category of light components in asphalt. The incorporation of DOP supplements the light components of asphalt and increases the content of volatile and decomposable components that can be supplied in the first stage of quality loss, resulting in a decrease in the thermal stability of the sealant. In Figure 5(c), the remaining percentage mass of the total system decreases due to the more volatilization of the sealant with a larger amount of DOP in the first stage and the increase of the mass reduction percentage.

The thermogravimetric results of the asphalt and the sealant under four heating rates of 5 K/min, 10 K/min, 15 K/min, and 20 K/min were analyzed to further explore the influence of DOP on the thermal stability of the sealant. The activation energy  $E_a$  of the five samples was calculated by (1) based on the obtained maximum rate decomposition temperature  $T_{max}$  [30], and the calculation results are shown in Table 7.

$$\ln \frac{\beta}{T_{max}^2} = \ln \frac{AR}{E_a} - \frac{E_a}{RT_{max}}, \quad (1)$$

where  $\beta$  is the heating rate,  $\text{K}\cdot\text{min}^{-1}$ ;  $T_{max}$  is the temperature when DTG reaches the maximum value, K;  $A$  is the frequency factor,  $1\cdot\text{s}^{-1}$ ;  $E_a$  is the apparent activation energy,  $\text{J}\cdot\text{mol}^{-1}$ ;  $R$  is the ideal gas constant,  $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

Generally speaking, a higher activation energy indicates that the chemical reaction has a higher barrier, that is, the more difficult the chemical reaction is to occur. It is shown that the more energy needs to be consumed in the process of mass loss under high-temperature conditions for asphalt system materials. Therefore, a difficult volatilization and decomposition process indicates a better thermal stability. It can be seen from Table 7 that the activation energy of the sealant without DOP is significantly increased compared with the asphalt, which indicates that the thermal stability of the sealant is much better than that of the asphalt. In addition to the swelling effect of the SBS modifier absorbing the light components of the asphalt, the main reason is the effect of the stabilizer in the sealant.

On the one hand, the addition of stabilizers has a certain effect on improving the compatibility between the modifier and the asphalt. On the other hand, the essence of stabilizers to slow down the chemical reaction and maintain chemical balance is to increase the activation energy of the reaction. Therefore, the activation energy of the sealant is significantly improved compared with that of the asphalt. The activation energy of the sealant is significantly reduced with the incorporation of DOP, but the amount of DOP has little effect

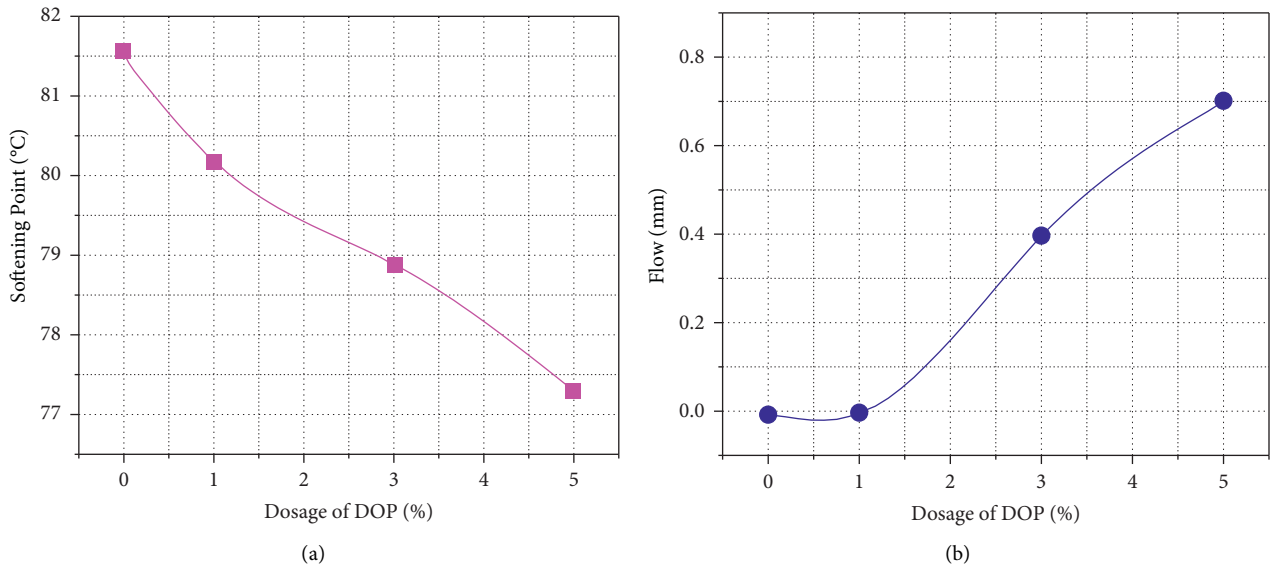


FIGURE 3: Effect of DOP dosage on the high-temperature performances of sealant: (a) softening point; (b) flow.

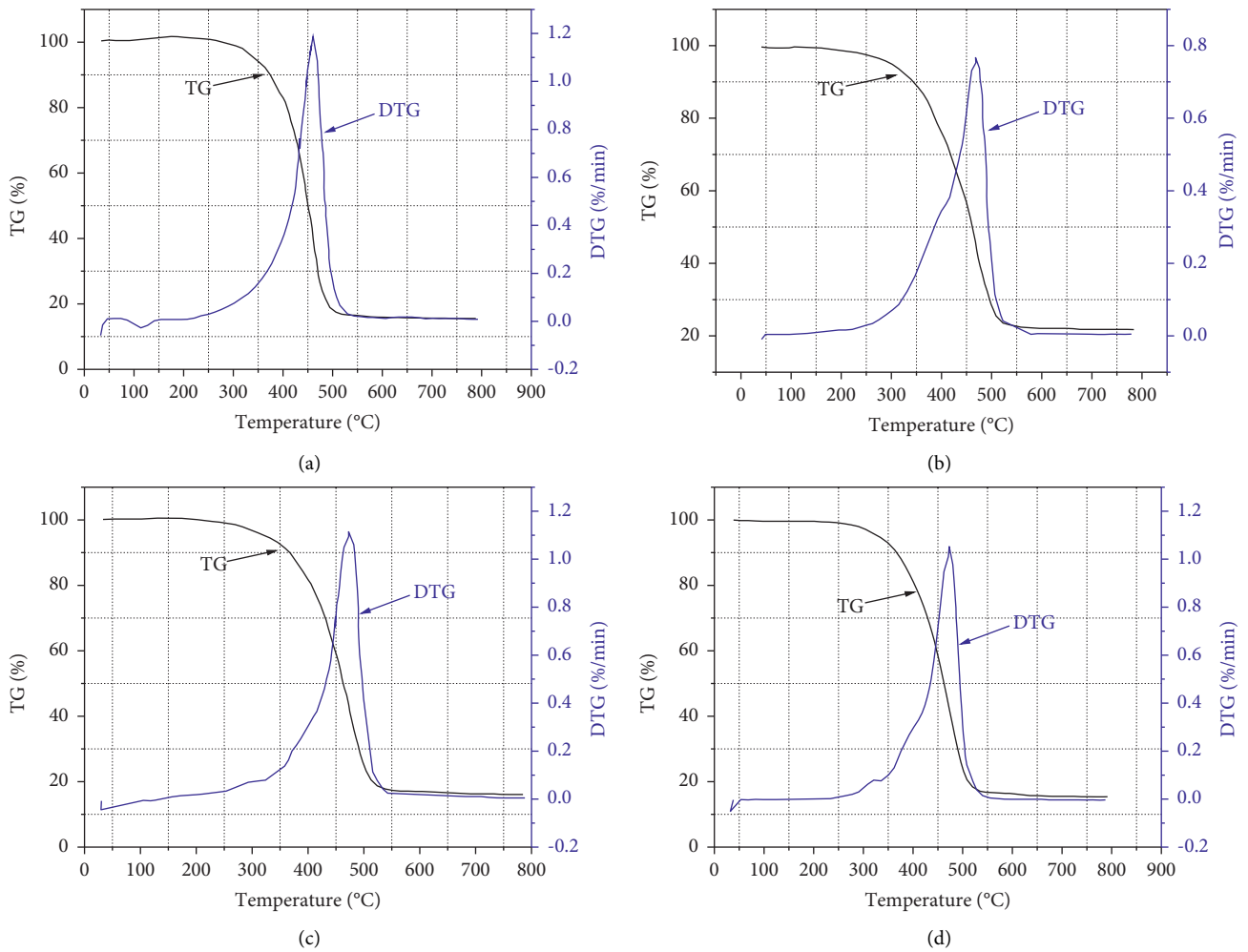


FIGURE 4: Continued.

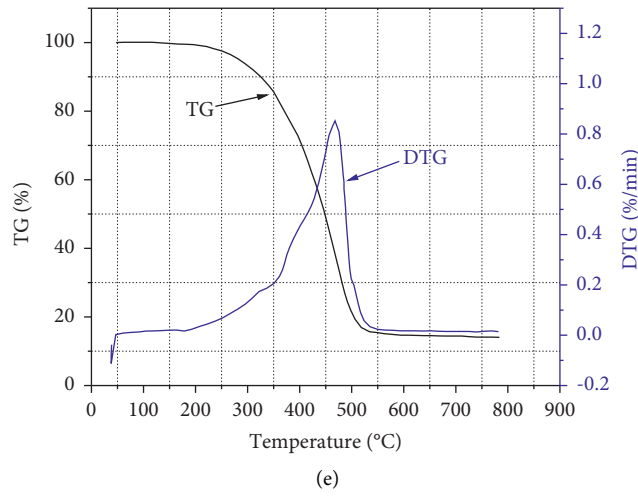
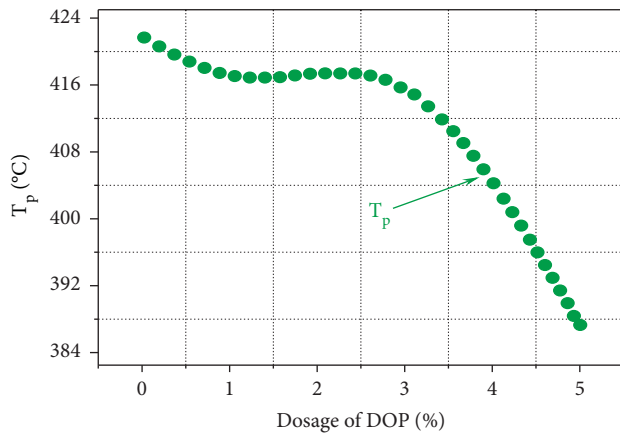


FIGURE 4: TG-DTG curves of samples: (a) asphalt; (b) sealant without DOP; (c) sealant with 1% DOP; (d) sealant with 3% DOP; (e) sealant with 5% DOP.

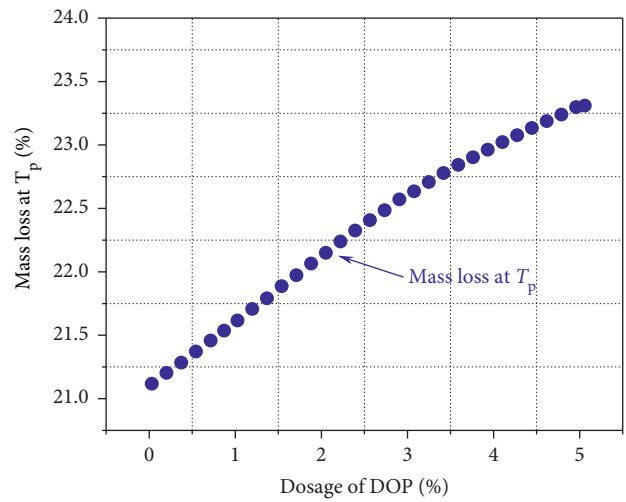
TABLE 6: TG-DTG results of asphalt and sealant without DOP.

Samples	$T_p$	Quality loss at $T_p$ (%)	Remaining mass (%)
Asphalt	403.1	19.1	15.0
Sealant without DOP	421.8	21.1	21.6

Note.  $T_p$  is the extrapolated starting temperature of the mass loss; the remaining mass is the remaining mass when reaching the maximum temperature.



(a)



(b)

FIGURE 5: Continued.

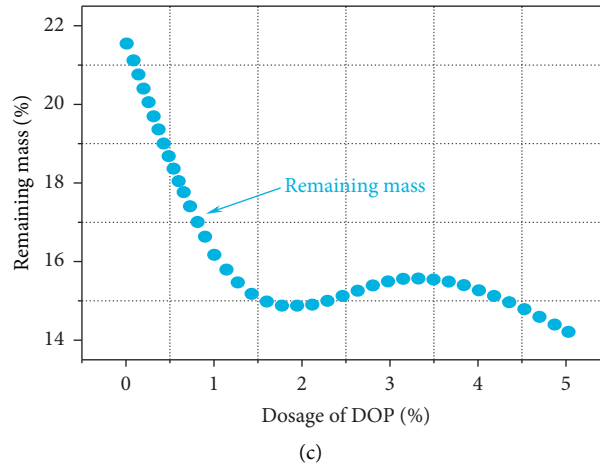


FIGURE 5: Relationship between DOP content and various parameters: (a)  $T_p$ ; (b) mass loss at  $T_p$ ; (c) remaining mass.

TABLE 7: Apparent activation energy of 5 samples ( $E_a$ , kJ/mol).

Asphalt	Sealant with different dosages DOP			
	0%	1%	3%	5%
32.8	101.4	55.3	55	50.8

on the activation energy. The activation energy of the sealant with 5% DOP is still higher than that of the asphalt, which shows that DOP is slightly detrimental to the thermal stability of the sealant. In all, it can be concluded that the degradation of DOP on the high-temperature performance of sealant is still within the acceptable range.

### 3.2. Low-Temperature Performance

**3.2.1. Low-Temperature Stretch Length.** In Figure 6, the low-temperature stretch length of the sealant increases significantly with the increase of DOP content, which shows that DOP can significantly improve its low-temperature performance. This is mainly because on the one hand, DOP can increase the internal light components of the sealant as discussed in Section 3.1.1, which can enhance the internal fluidity of each component and significantly increase the overall stretch length of the sealant. On the other hand, the interaction between the highly polar ester group and the asphaltene in DOP can weaken the cross-linking between the polymer and the asphaltene molecules, thus enhancing the mobility of the polymer molecules and improving the low-temperature performance of the sealant.

**3.2.2. Glass Transition Temperature.** The low-temperature DSC tests were carried out on the sealant with different DOP content to further explore the influence of DOP content on the low-temperature performance of the sealant. Figure 7 shows the DSC curves of the sealant with different DOP content. In Figure 7, the sealant with different DOP content shows an endothermic state in the temperature range of  $-60$ – $40^\circ\text{C}$ . The relatively consistent endothermic curves of the four samples indicate that their phase transition modes

are the same, reflecting that the existence of sealant has not changed significantly, but the detailed mechanism of DOP and sealant still needs to be verified by FTIR in Section 3.3.1.

The glass transition temperature of the sample was calculated according to the curves in Figure 7, and the results are shown in Figure 8. In Figure 8, the glass transition temperature of the sealant gradually decreases with the increase of DOP content, which means that the sealant can still maintain viscoelastic state under low-temperature conditions without brittle fracture. This indicates DOP can improve the low-temperature performance of sealant. In addition, there was a significant difference in the low-temperature performance of sealant mixed with DOP and without DOP. The glass transition temperature of sealant without DOP was  $-16.1^\circ\text{C}$ . This shows that the viscoelasticity of the sealant drops sharply because the sealant has completely transformed into a glass state and is prone to brittle fracture under the low-temperature tensile test environment at  $-20^\circ\text{C}$ . The glass transition temperature of the sealant with 1% DOP dropped below  $-20^\circ\text{C}$ , so its low-temperature stretch length was greatly increased, as shown in Section 3.2.1. In short, the glass transition temperature of sealant is further reduced with the increase of DOP content, and thus the low-temperature performance is further improved.

### 3.3. Mechanism Analyses

**3.3.1. Infrared Spectrum Analysis.** Figure 9 shows the infrared spectra of asphalt and the sealant without DOP. For asphalt, the strong vibration peaks at  $2846.1\text{ cm}^{-1}$  and  $2913.25\text{ cm}^{-1}$  are associated with the stretching vibrations of the C-H bonds on saturated carbon atoms. The peak of band at  $1631.93\text{ cm}^{-1}$  is associated with the stretching vibration of



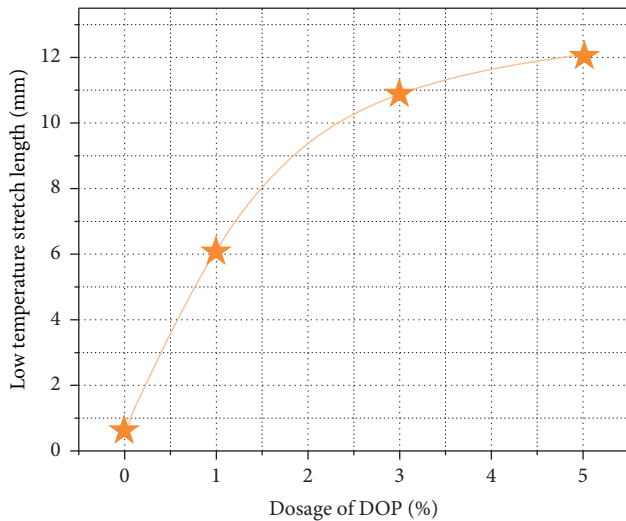


FIGURE 6: Influence of DOP content on stretch length of sealant at low temperature.

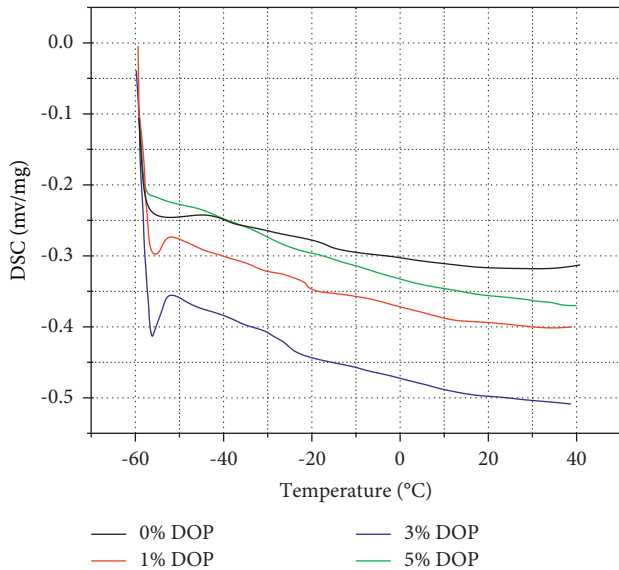


FIGURE 7: DSC curves of sealant with different DOP content.

the C=C double bond of mononuclear aromatic hydrocarbon. In the fingerprint region, the peak of band at  $1445.91\text{ cm}^{-1}$  and  $1373.04\text{ cm}^{-1}$  is the bending vibration of methylene C-H bond and symmetrical bending vibration of methyl C-H on the saturated carbon atom, respectively. In addition, the peaks at  $814.39\text{ cm}^{-1}$  and  $747.24\text{ cm}^{-1}$  are defined by the out-of-plane bending vibrations of the C-H bond on benzene ring.

In Figure 10, there is a new peak for the sealant without DOP at  $618.6\text{ cm}^{-1}$ , which is associated with the out-of-plane bending vibration of the alkyne C-H bond. It can be caused by the chemical reaction between the rubber powder and substances in the system. Similarly, the peak value of  $698.66\text{ cm}^{-1}$  of the sealant without DOP can be due to the out-of-plane bending vibration of C-H bond on the benzene ring. It is worth noting that there is a new peak at

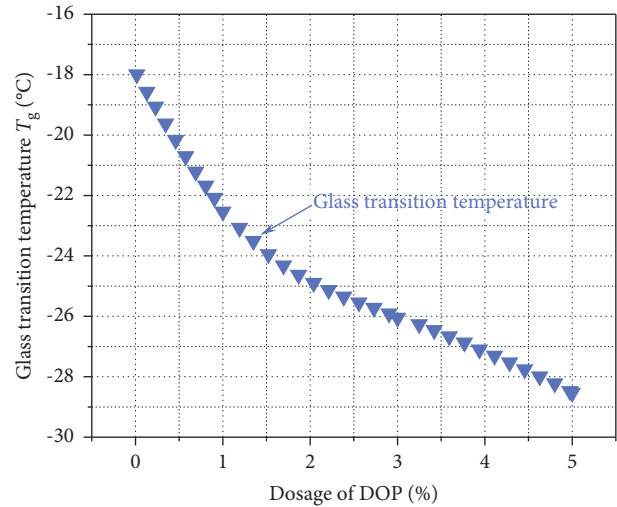


FIGURE 8:  $T_g$  of sealant with different DOP content.

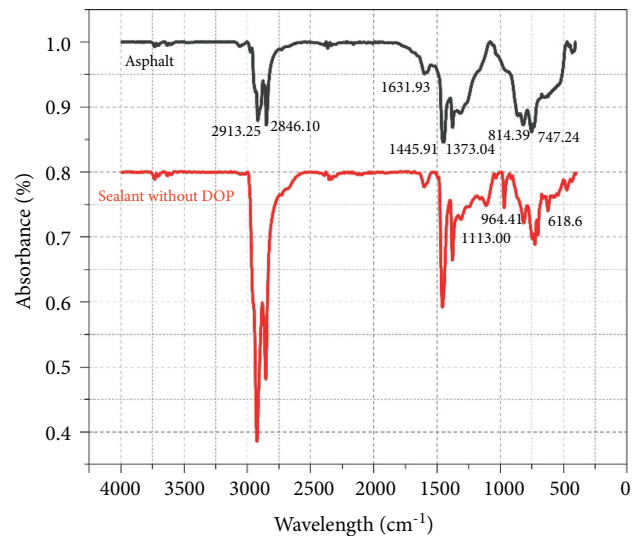


FIGURE 9: Infrared spectra ( $400\text{--}4000\text{ cm}^{-1}$ ) of asphalt and the sealant without DOP.

$1113.00\text{ cm}^{-1}$ , which is attributed to the in-plane bending vibration of the C-H bond on the benzene ring. This is because the sealant contains rubber oil mainly based on aromatic bases, so there are more benzene ring C-H bonds in the sealant without DOP compared with asphalt. And there is a new peak at  $964.41\text{ cm}^{-1}$ , which is due to the C-H bending vibration of the butadiene double bond in SBS molecular chain in the sealant without DOP. In addition, no other miscellaneous peaks were found in the infrared spectrum of sealant, which shows that there is no evident chemical reaction between the asphalt and modifier, and the raw materials in sealant are mainly physically modified to the asphalt.

In Figure 11, a new peak at  $1725.37\text{ cm}^{-1}$  in sealant mixed with DOP was founded. This is a characteristic peak of DOP molecule, which is attributed to the stretching vibration of the C=O double bond in the ester compound. In

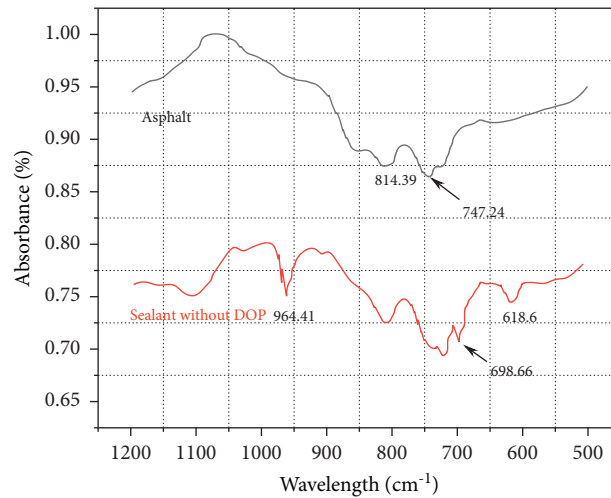


FIGURE 10: Infrared spectra (500–1200  $\text{cm}^{-1}$ ) of asphalt and the sealant without DOP.

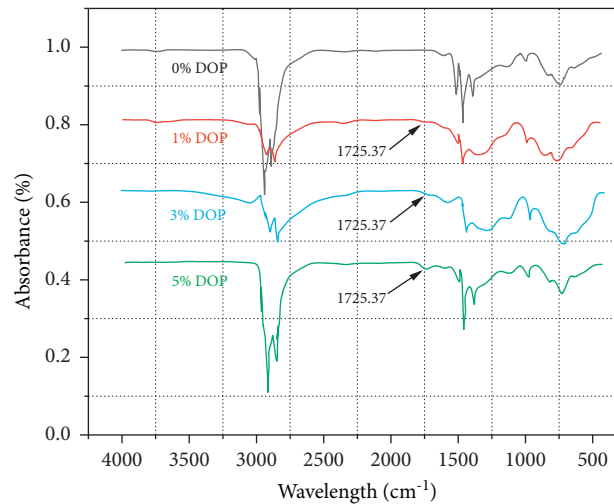


FIGURE 11: Infrared spectra (400–4000  $\text{cm}^{-1}$ ) of sealant with different DOP content.

addition, no other characteristic peaks were found. Therefore, it is further proved that there is no evident chemical reaction between DOP and asphalt molecules, and the plasticizing effect of DOP mainly comes from physical effects.

**3.3.2. Compatibility Analyses.** The microscopic morphologies of the four samples under 400 times magnification are shown in Figure 12. In Figure 12(a), there is no substance that can produce fluorescence in the asphalt, so the image appears blank. In Figure 12(b), the polymer particles in sealant without DOP are evenly and densely distributed in spherical or linear

shapes. And the outline of the polymer particles is clear, which indicates that the polymer does not form a good correlation structure with asphalt due to the poor compatibility between the polymer and the asphalt. In Figure 12(c), it can be seen that more polymer particles swell slightly and change from spherical to linear after adding 1% DOP. The expanded polymer particles begin to join together as a whole, indicating that the polymer has better compatibility with asphalt. This is due to the fact that DOP as a plasticizer can intersperse between polymer molecules to increase the flexibility and improve compatibility for polymer. In addition, it can be seen from Figure 12(d) that the polymer is completely compatible with asphalt after adding 5% DOP.

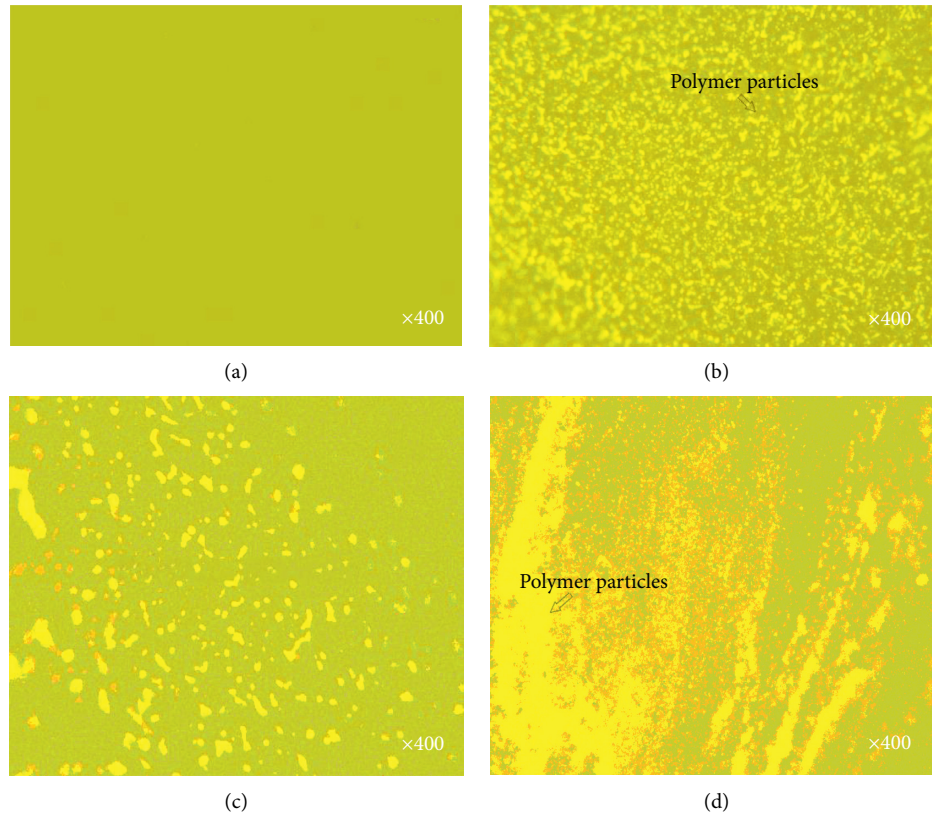


FIGURE 12: Micro morphology of the samples under 400 times magnification: (a) asphalt, (b) sealant with 0% DOP, (c) sealant with 1% DOP, and (d) sealant with 5% DOP.

#### 4. Conclusions

In this work, effects of DOP content on the thermal stability and low-temperature performance of asphalt sealants were investigated. Thermal stability was evaluated by flow, softening point and TG-DTA results, and low-temperature performance was reflected by low-temperature tensile length and glass transition temperature. In addition, the mechanism of DOP on sealant properties was also explored. The following conclusions can be drawn based on the experimental results.

- (1) The low-temperature performance of asphalt sealant was successfully evaluated based on the self-designed stretch fixture, which possesses the following advantages: the stretch length can be accurately measured to quantitatively evaluate the low-temperature performance of sealant; the improved stretch fixture is reasonable with its low cost, simple operation, and high testing efficiency.
- (2) DOP can slightly deteriorate the thermal stability of sealant within acceptable range. The softening point of the sealant with DOP decreases and the flow increases, but the softening point and apparent activation energy of the sealant with high DOP content are still much larger than asphalt, indicating the degradation of DOP on the high-temperature performance of sealant is still within the acceptable range.
- (3) The low-temperature performance of sealant can be greatly improved after adding DOP. The

low-temperature stretch length of the sealant with DOP is increased and the glass transition temperature decreased significantly, which is due to the fact that DOP can increase the light components of sealant and enhance the internal fluidity of each component.

- (4) There is no evident chemical reaction between DOP and asphalt molecules, and the plasticizing effect of DOP mainly comes from physical effects. The polymer in the sealant gradually expanded and crosslinked with the increase of DOP content. The polymer can be completely compatible with the asphalt with 5% DOP. Therefore, DOP can enhance the compatibility between the asphalt and polymer molecules.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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