

Research Article

Study on Epoxy Resin-Modified Asphalt Binders with Improved Low-Temperature Performance

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Epoxy resin-modified asphalt binder (ERMAB) has been widely used in the pavement of steel bridges, while the improvement on its low temperature is still a big challenge to researchers. This paper tries to improve the low-temperature performance of ERMAB by optimizing the modifier, epoxy resin. Firstly, three epoxy resins and three amine curing agents were prepared and used for the modification of asphalt binders. Secondly, the formula and prepared methods of ERMABs were optimized and determined through compatibility, viscosity growth rate, and tensile tests. Thirdly, an overall comparison on the phase structure, thermal stability, low-temperature performance, temperature and frequency dependence, and fatigue performance of prepared ERMABs and control sample were made. Results show that polyurethane-modified epoxy resin or dimer acid-modified epoxy resin, with a suitable curing agent, can significantly improve the low-temperature performance of ERMAB, and the curing time meets the construction requirements. Compared with the control sample, the two ERMABs have basically the same rheological properties at medium temperature, but slightly worse high-temperature performance and fatigue resistance. The significance of this paper lies in proposing a feasible way to improve the low-temperature performance of ERMAB.

1. Introduction

Epoxy resin asphalt concrete is one of the mainstream construction forms for steel bridge deck paving. Compared with grouting asphalt concrete and SMA asphalt concrete, epoxy resin asphalt concrete, made from epoxy resin modified asphalt binder (ERMAB) and aggregates, possesses better stiffness, strength, impact resistance, and abrasion resistance and is widely employed in pavement of cross-river bridges at home and abroad [1–3]. Therefore, continuous efforts have been made to explore high-performance ERMAB.

Cong et al. [4] studied the effect of epoxy resin on improving the rheological properties of matrix asphalt binder and found that epoxy resin can not only significantly improve its high-temperature performance but also reduce its creep behavior and enhance its recovery ability. Yu et al.

[5] further studied the improvement effect of epoxy resin on SBS-modified asphalt binder from the aspects of viscosity growth, microscopic morphology, high-temperature performance, and mechanical properties. Their studies have proved that the modified asphalt binder with a suitable formula can meet the requirements of construction specifications, and its mechanical properties and rutting resistance have been significantly improved. Kang et al. [6] further compared the rheological properties of ERMAB, matrix asphalt binder, and SBS-modified asphalt binder and confirmed the above research results. Similarly, the follow-up studies of Yin and Cong [7, 8] also confirmed the conclusions of the abovementioned researchers and the feasibility that ERMAB could be applied to pavement construction of steel bridges. Gong et al. [9] studied the comprehensive performance of ERMAB mixed with waste rubber powder and Sasobit and concluded that the addition

of Sasobit could offset the negative effects of viscosity increase caused by the addition of waste rubber powder and reduce average particle size and continuous area fraction of waste rubber powder. Jiang et al. [10] studied the micro-morphology and macromorphology changes of epoxy asphalt binder modified by brominated SBS, explained the curing principle of the new modifier, and considered the epoxy asphalt binder modified by brominated SBS as an environmental-friendly material. In the study of Xin et al. [11], lignin and tung oil was used to prepare epoxy resin, which was further adopted to modify asphalt binder. The effectiveness of this new and environmental-friendly method has been affirmed by studying the performance of the above ERMAB. Qian et al. [12] studied the improvement effect of mineral fiber on epoxy asphalt binder in low-temperature crack resistance and resistance to fatigue cracking and found that the wear resistance of the modified asphalt binder was also enhanced.

It can be known from above studies that researchers have reached a consensus on the good application of ERMAB in pavement of steel bridges. Meanwhile, these results also reveal that the current research on epoxy resin asphalt binder is relatively dispersed and has not formed a system. Their research mainly focuses on the improvement of epoxy resin on the high-temperature performance and fatigue performance of asphalt binders, and the introduction of high-performance admixtures. However, there is still no systematic study on methods to improve the poor low-temperature performance of epoxy resins and ERMABs. In fact, compared with other modified asphalt binders, ERMAB, with thermosetting epoxy resin as modifiers, exhibits worse flexibility at low temperatures, which greatly narrow its application in practical construction [6, 13, 14]. Therefore, improving the low-temperature performance of ERMAB without increasing the difficulty of construction is a problem worthy of study. This paper tries to improve the low-temperature performance of ERMAB by adopting the low-temperature-improvement epoxy resin as the modifier. Specifically, polyurethane-modified epoxy resin (U), dimer acid-modified epoxy resin (D), silicone rubber-modified epoxy resin (S), and three self-made amine curing agents (*P*, *Q*, and *R*) were prepared and used to modify asphalt binder firstly. Then, the formula and prepared methods of ERMABs were further studied and determined. Finally, a comprehensive performance, including phase structure, thermal stability, low-temperature performance, dependence on temperature and frequency, and fatigue performance of prepared ERMABs were studied and compared with the control sample.

2. Raw Materials and Experimental Methods

2.1. Raw Materials

2.1.1. Epoxy Resin. In this paper, bisphenol-A-epoxy resins, E51, as the most common epoxy resin, is used as a control sample. Three types of low-temperature-modified epoxy resin are prepared, namely, polyurethane-modified epoxy resin (U), dimer acid-modified epoxy resin (D), and silicone

rubber-modified epoxy resin (S). These four types of epoxy resin are used as modifiers to form modified asphalt binders (EA, UA, DA, and SA), and their performance is compared and evaluated in this paper. It should be noted here that the ratio of the E51 and curing agent used for the modified asphalt binder is the best ratio recommended by the manufacturer.

2.1.2. Curing Agent. The curing agents used in this paper are amine curing agents, which are all self-made, namely, *P*, *Q*, and *R*, with their curing efficiency ranging from low to high. In this part, curing time, tensile strength, and elongation at break are used to determine optimal agents. Figure 1 shows the self-made modified epoxy resin and curing agents.

2.1.3. Matrix Asphalt Binder. Relevant studies have shown that the content of asphaltene in asphalt binder is positively correlated with the compatibility of epoxy resin [7,15]. Therefore, considering the purpose of improving the low-temperature performance of ERMAB in this paper, we adopt A-70 matrix asphalt binder, and its basic performance is shown in Table 1.

2.2. Preparation of ERMABs. The raw materials include epoxy resins, curing agents, and matrix asphalt binder. Firstly, we preheated the epoxy resins in an oven for 1 hour at 85°C and the matrix asphalt binders for 3 hours at the curing temperature. Secondly, epoxy resins and curing agents were mixed at target ratios at 500 rpm for 5 minutes at 85°C in a 250 ml beaker to obtain compound epoxy resins. Thirdly, compound epoxy resins and matrix asphalt binders were mixed at 500 rpm for 25 min at the curing temperature to obtain ERMABs. It is worth noting that the epoxy resins are represented by U, D, S, and E51, respectively, while the prepared ERMABs is represented by UA, DA, SA, and EA to avoid confusion.

2.3. Experimental Methods. Experimental methods in this paper are different from the traditional modified asphalt binder test method, since the ratio of epoxy resin to asphalt binder should be assumed firstly so as to determine factors such as the ratio of epoxy resin to curing agent. In this experiment, firstly, in accordance with laboratory experiments routine and related references [16, 17], the ratio of epoxy resin to asphalt binder is assumed to be 40:60 by weight, based on which the type of epoxy resin, type and optimal dosage of curing agent, and the curing temperature are selected. Secondly, the optimal ratio of epoxy resin to asphalt binder is determined by changing dosages. Finally, according to the obtained formula of ERMABs, their comprehensive performance is studied and the reasons are analyzed. Also the comparisons with the performance of the control sample are made.

2.3.1. Compatibility Test. The purpose of this test is to determine appropriate epoxy resin, and observation methods are used. First, the prepared mixture of epoxy resin and hot matrix asphalt binder were stirred at 120°C for 5 minutes at a

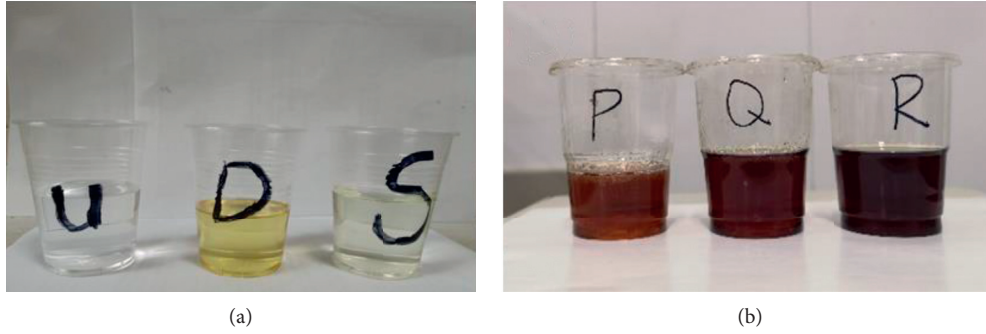


FIGURE 1: The appearance of self-made modified epoxy resins (a) and curing agents (b).

TABLE 1: Basic performance of A-70 matrix asphalt binder.

Items	A-70 matrix asphalt binder		
	Results	Index	
Penetration (25°C, 100 g, 5 s)/0.1 mm	74.0	60-80	
Ductility (15°C, 5 cm/min)/cm	>120	>100	
Softening point (ring and ball method)/°C	47.4	≥46	
Solubility (%)	99.90	>99.5	
Residue after RTFOT	Quality change (%) Penetration ratio (%)	−0.1 73	≤±0.8 ≥61
Relative density of asphalt at 25°C/(g/cm ³)	1.031	—	

ratio of 40:60. Next, we dropped some mixture with a glue-tip dropper onto the prepared glass slide, covered it with a cover glass, and placed it in an oven at 120°C for 60 minutes. Finally, we took out the sample and studied the compatibility of the epoxy resin and the asphalt binder after it cooled to room temperature.

2.3.2. Viscosity Test. After determining the type of epoxy resin, it is necessary to select the appropriate curing agent type and dosage and curing temperature to achieve the most favorable conditions for engineering applications. The viscosity increase and mechanical properties of ERMABs during the curing processes are the main evaluation index, so the viscosity test and tensile test are employed to detect this variation.

For the viscosity test, Brookfield viscometer was adopted. The rotor was no. 27, and the speed was 50 r/min. The specific test procedures were carried out in accordance with ASTM D2393 specification [18], and we recorded once every minute continuously until the viscosity reaching 5000 MPa·s or the test time reaching 90 minutes. The times when the viscosity were increased to 1000 MPa·s and 3000 MPa·s were particularly concerned.

2.3.3. Tensile Test. The tensile test was carried out based on ASTM D638 specification [19]. Six sets of replicas were measured at the specified temperature of 23°C for each binder, and the evaluation indexes were tensile strength and elongation at break. The details of test samples and test processes are shown in Figure 2.

2.3.4. Microscopic Fluorescence Test. During the microscopic fluorescence test, microscopic morphology and phase structure of the epoxy resin and matrix asphalt binder within the ERMABs are observed, which could better explain the changes in its macroscopic properties. In this test, the cured ERMABs were used to make glass slide samples, which were observed in blue light in the case of 100-fold magnification with a fluorescence microscope.

2.3.5. Thermogravimetric Analysis (TGA). The TGA test mainly analyzes the thermal decomposition of the internal substances of ERMABs. In this test, the mass of the sample was 10 mg, the test temperature was in the range of 25°C to 900°C, the heating rate was 10°C/min, and the protective gas was nitrogen.

2.3.6. Ductility Test. The ductility test was used to evaluate the low-temperature performance of three prepared ERMABs and the control samples. The test was carried out in accordance with ASTM D113 specification [20]. The test temperature was 5°C and 10°C, the extension speed was 5 cm/min, and the evaluation index was extension length.

2.3.7. Bending Beam Rheometer (BBR). BBR was also employed to evaluate the low-temperature performance of ERMABs. The BBR test was carried out in accordance with ASTM D6373 specification [21]. The test temperature was −6°C, −12°C, −18°C, and −24°C. The evaluation indexes were stress relaxation speed (m) and creep stiffness modulus (S). At least three samples of every modified asphalt binder were tested. The calculation formula of evaluation indexes is shown in

$$S(t) = \frac{PL^3}{4bh^3\delta(t)}, \quad (1)$$

$$m = \frac{dlgS(t)}{dlgt}, \quad (2)$$

where $S(t)$ refers to the creep stiffness modulus (MPa). m refers to the stress relaxation speed. P refers to the constant load (N) at the midpoint of the sample. L , b , and h refer to the distance between the support points of the beam, the height of the beam, and the width of the beam, respectively.



FIGURE 2: Dumbbell shape (a) and tensile details (b) of the test samples.

$\delta(t)$ refers to the deflection (mm) of the beam midpoint under load over time.

2.3.8. Temperature and Frequency Sensitivity Tests. Temperature sensitivity test and frequency sensitivity test, respectively, evaluate the dependence of ERMABs on temperature and frequency changes, both of which are carried out by using dynamic shearing rheometer. During the temperature sweep test, the test temperature range was from 30°C to 90°C, the frequency was 10 rad/s, and the shear strain was 5%. In the frequency sweep test, the test temperature was 15°C, 30°C, 45°C, and 60°C, the frequency was 0.1–100 Hz, and the shear strain was 2%. After the temperature sweep test, complex modulus G^* and phase angle δ were employed for evaluation. After the frequency sweep test, the frequency master curve was used for evaluation, and the master curve reference temperature was 30°C.

2.3.9. Multiple Stress Creep Recovery (MSCR). MSCR is used to evaluate the fatigue performance of ERMABs. The test was carried out in accordance with AASHTO MP19 specification, and the test temperature was 64°C [22]. Samples were tested for 10 cycles with pressures of 0.1 kPa and 3.2 MPa, respectively. After the test, the relationship curve between shear strain and time, the recovery rate (R), and non-recoverable recovery creep compliance (J_{nr}) in the deformation were used to analyze the results. The calculation equations of R and J_{nr} are shown in

$$R = \frac{\gamma_p - \gamma_{nr}}{\gamma_p - \gamma_0}, \quad (3)$$

$$J_{nr} = \frac{\gamma_{nr} - \gamma_0}{\tau}, \quad (4)$$

where γ_p refers to the peak shear strain of each loading cycle. γ_{nr} refers to the residual shear strain of each loading cycle. γ_0 refers to the initial shear strain of each loading cycle.

3. Formula and Prepared Methods of ERMABs

3.1. Epoxy Resin. Figure 3 shows the results of the compatibility test of epoxy resin E51, U, D, and S and matrix asphalt binders. It can be seen that in the test S and matrix asphalt binders were obviously segregated, while U, D, and E51 were not. The reason is that S is modified by silicone

rubber. The calculated solubility parameter of silicone rubber is $7.65 (\text{J}/\text{cm}^3)^{1/2}$, while the solubility parameter of matrix binder is $15.68 (\text{J}/\text{cm}^3)^{1/2}$, and the large difference between the two leads to poor compatibility [23,24]. Therefore, S will no longer be used in subsequent experiments.

3.2. Curing Agent

3.2.1. Types of Curing Agent. As mentioned before, the optimization of curing agent P, Q, and R was determined by comparing viscosity growth rates, tensile strength, and elongation at break of different ERMABs.

Figure 4 shows the viscosity-time increasing curves of UA and DA with curing agent P, Q, and R. In these results, the ratio of curing agent to U was 1 to 9, and the ratio of curing agent to D was 1 to 21 according to laboratory experience. It can be seen that the curing processes of ERMABs with Q and R were obviously faster. In terms of DA, when the curing agent was R, the viscosity of the ERMAB reached 1000 MPa·s after 35 minutes and 3000 MPa·s after 51 minutes; when the curing agent was Q, the viscosity reached 1000 MPa·s after 46 minutes, and reached 3000 MPa·s after 61 minutes; when the curing agent was P, the viscosity reached 1000 MPa·s after 56 minutes and reached 3000 MPa·s after 73 minutes. As for UA, the viscosity of ERMABs with curing agent increased even faster. When the curing agent was P, the viscosity reached 1000 MPa·s after 54 minutes and reached 3000 MPa·s after 67 minutes. It is known that during the actual construction, a faster viscosity growth rate means a shorter residence time, which will cause additional difficulties, so sufficient time for construction is essential. Researchers believed that it is appropriate the viscosity of the ERMAB reaches 1000 MPa·s after 50 minutes [25]. According to this specification, the comparison results show that P meets the requirements as a curing agent for both UA and DA.

Figure 5 shows different ERMABs have similar changes overall. In terms of tensile strength, the tensile strength of ERMABs with curing agents P and R was quite similar. In contrast, the tensile strength of that with curing agent Q was lower. In terms of elongation at break, the ERMAB prepared with curing agent Q the largest, followed by P and R.

Based on the results of the viscosity test and tensile test, it can be considered that the curing agent P has advantages in terms of viscosity growth rate, tensile strength, and

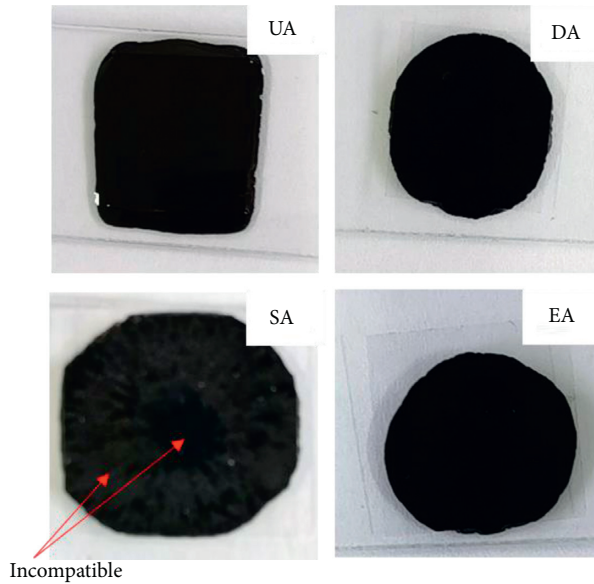


FIGURE 3: Results of compatibility test of UA, DA, SA, and EA.

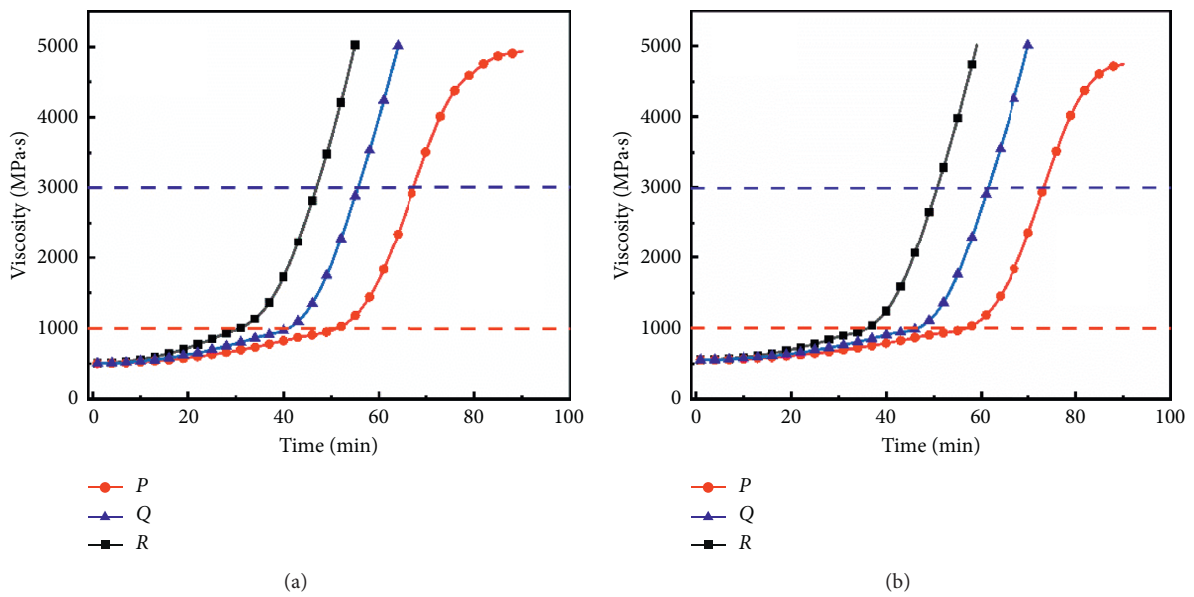


FIGURE 4: Viscosity-time curves of UA (a) and DA (b).

elongation at break. Therefore, curing agent P will be adopted for subsequent experiments.

3.2.2. Dosage of Curing Agent. After determining the type of curing agent, the dosage of curing agent needs to be further studied. As mentioned earlier, the experiment was carried out on the assumption that the ratio of epoxy resin to matrix asphalt binder was 40 to 60 by weight. Herein, ERMABs were prepared in the conditions that the ratio of epoxy resin U to curing agent P was 8 to 1, 9 to 1, and 10 to 1, and the ratio of epoxy resin D to curing agent P was 20 to 1, 21 to 1, and 22 to 1 by weight, respectively. Finally, viscosity growth and tensile test results were analyzed.

Figure 6 shows the viscosity growth curves of ERMABs with different dosages of curing agents. Although with different epoxy resins, these two types of ERMABs have the similar curves. When the dosage of curing agent P was high, that is, when the ratio of U to P was 8 to 1 and D to P was 20 to 1, both ERMABs had faster curing speeds and shorter time it took to increase the viscosity to 1000 MPa·s and 3000 MPa·s. When the dosage of curing agent P was low, that is, when the ratio of U to P was 10 to 1 and D to P was 22 to 1, the viscosity of the two binders increased more slowly. Especially for DA, the viscosity could hardly increase to the relatively high value within the test time, which may decrease the mechanical properties of prepared binders. When the amount of curing agent P was moderate, that is, when the ratio of U to P was 9 to

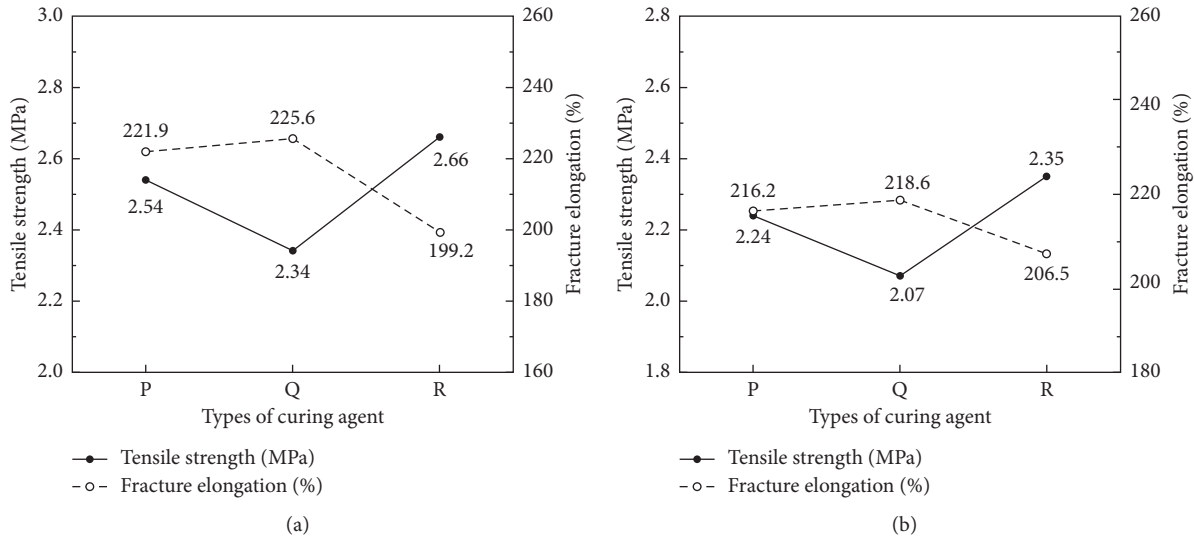


FIGURE 5: Tensile test results of UA (a) and DA (b) at 23°C.

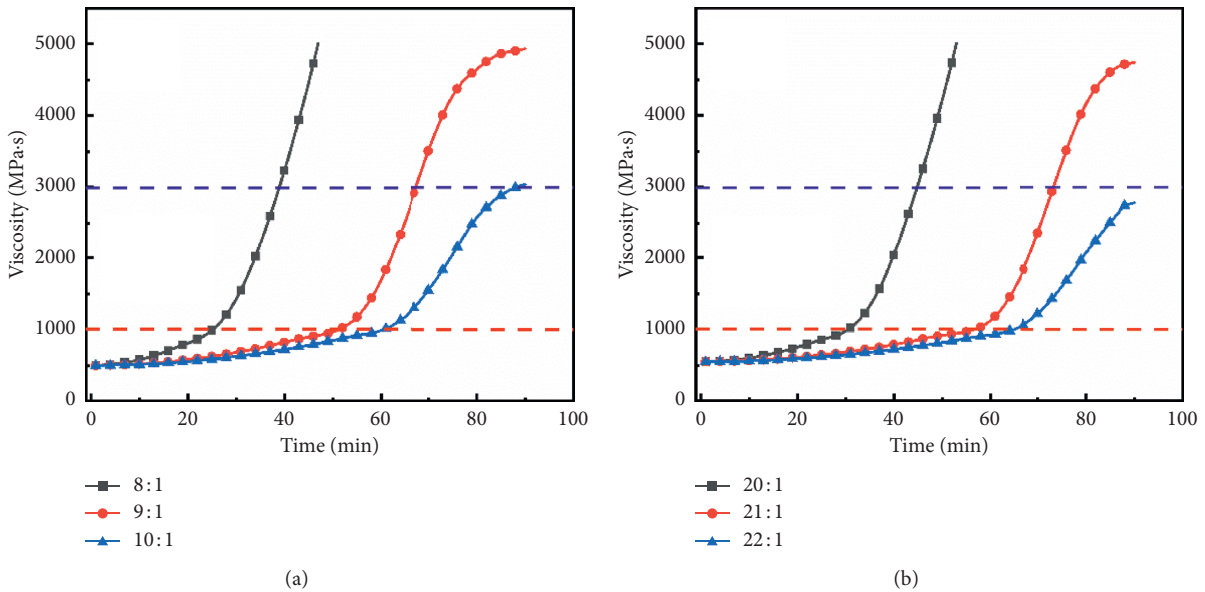


FIGURE 6: Viscosity-time curves of UA (a) and DA (b) with different dosages of curing agent.

1 and D to P was 21 to 1, the viscosity growth rate was also moderate, and the curing time was reasonable.

The curves in Figure 7(a) show that as the dosage of curing agent gradually decreased, the tensile strength decreased, and the elongation at break gradually increased. When the ratio of U to P was changed from 8 to 1 to 9 to 1, the tensile strength decreased by 3.8% and the elongation at break increased by 9.6%. When the ratio of U to P changed from 9 to 1 to 10 to 1, the tensile strength of the asphalt binder was significantly reduced, and the reduction rate reached 21.1%, while the elongation at break increased by 4.4%. Therefore, it reflected that when the dosage of curing agent is too low, the tensile strength of the ERMAB will be greatly affected. Similarly, the similar conclusion could be obtained from Figure 7(b).

Based on the above analysis, it can be concluded that the most appropriate ratios of U to P and D to P are 9 to 1 and 21 to 1 by weight, respectively.

3.3. Curing Temperature. The previous sections have studied the types and dosages of curing agents, and this section will focus on curing temperature. Curing temperature mainly affects the reaction speed of the epoxy resin and the curing agent, which determines the residence time of the ERMABs during the construction process. First, ERMABs were prepared, in the conditions that the ratio of epoxy resin to matrix asphalt binder was 40 to 60, U to P was 9 to 1, and D to P was 21 to 1 by weight. Then, viscosity growth rates were

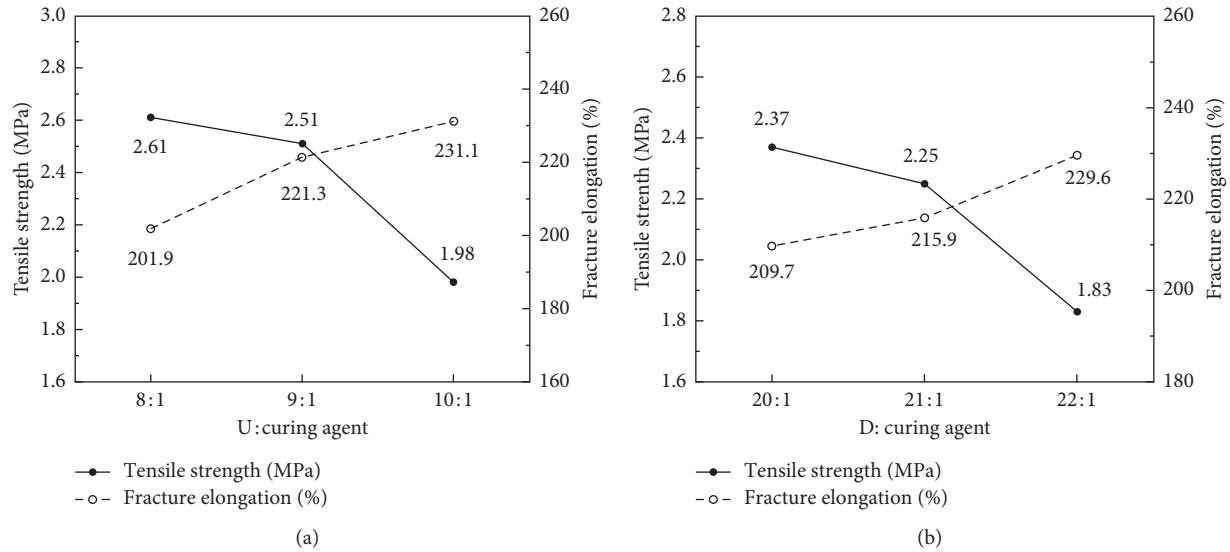


FIGURE 7: Tensile tests results of UA (a) and DA (b) with different dosages of curing agent.

studied when the curing temperature was 110°C, 120°C, and 130°C, respectively.

Figures 8(a) and 8(b) show similar changes of curves. When the curing temperature was 130°C, the viscosity increases rapidly, reaching 1000 MP·s within 20 minutes and 3000 MP·s within 40 minutes, which does not meet the actual construction requirements. When the curing temperature dropped to 120°C, the viscosity increase slowed down, and it took about 50 to 55 minutes to reach 1000 MP·s, and about 70 min to reach 3000 MP·s. When the curing temperature continued to decrease to 110°C, more time was needed to reach 1000 MP·s, and then viscosity increased too slowly and hardly reach 3000 MP·s during the test time. Therefore, 120°C is considered the most appropriate curing temperature in the test.

3.4. Formula and Curing Time of ERMABs

3.4.1. Formula. The ERMAB is composed of curing agent, epoxy resin, and matrix asphalt binder. When the ratio of epoxy resin to curing agent is determined, ratios of the two to the matrix asphalt binders should be further studied. From Sections 3.1 to 3.3, the ratio of epoxy resin to matrix asphalt binder was assumed of 40 to 60 by weight. In this section, other two ratios, namely, 30 to 70 and 50 to 50, are adopted in the test to confirm the suitable ratio.

Figures 9(a) and 9(b) show similar changes of curves. When the ratio of epoxy resin to matrix asphalt binder was 50:50, the viscosity increased the fastest. When the above ratio was reduced to 40 to 60, the viscosity increased slightly slowed down and mainly decreased the reaction speed of binder within 1000 MP·s. When the ratio further dropped to 30 to 70, the increase of the entire viscosity slowed down significantly, making it difficult to reach the desired high viscosity for ensuring sufficient high-temperature stability of the prepared binder.

Figure 10 shows the tensile test results of ERMABs with different ratios of epoxy resin to matrix asphalt binder.

Figure 10(a) shows that when this ratio is 30 to 70, the overall tensile strength is the lowest and the elongation at break is the highest. When the ratio is increased to 40 to 60, the tensile strength is increased by 14.5% and the elongation at break decreased by 7.4%. When the ratio is further increased to 50 to 50, the tensile strength decreases slightly and the elongation at break increases slightly. This indicated the proper dosage of epoxy resin is critical to the modified binder system, and either higher or lower dosage may bring negative effects on the mechanical properties of binder. Similar changes are shown in Figure 10(b).

Based on the above test results, it is believed that when the ratio of epoxy resin U and D to asphalt binder is 40 to 60, the curing time of ERMABs in relatively low viscosity range is long, the tensile strength is relatively high, and the elongation at break exceeds 220%. This result meets the requirements of actual construction and application [25]. Therefore, the ratio of epoxy resin to asphalt binders is 40 to 60 by weight.

3.4.2. Curing Time. Considering that this experiment adopts modified epoxy resin and self-made amine curing agents, in this section, tensile tests are used to further study the best curing time of ERMABs, with the assumption that the curing time is 2 h, 4 h, and 6 h, respectively.

Figure 11 shows the tensile test results of ERMABs with different curing times. In Figure 11(a), within the period of 2 h to 4 h, the tensile strength increased by 30.6% and the elongation at break decreased by 4.6%, which indicates that the curing reaction of the system is still going on between 2 h and 4 h. Within the period of 4 h to 6 h, the tensile strength hardly increased, and the elongation at break decreased by 3.3%, which shows that the curing reaction is basically over. It is also worth noting that excessive curing time at relatively high temperature will also affect the low performance of modified asphalt binder for the obviously oxidative aging effect on the epoxy resin. So, it can be considered that the suitable curing time is 4 h from Figure 11(a). Similar conclusions can be obtained from Figure 11(b).

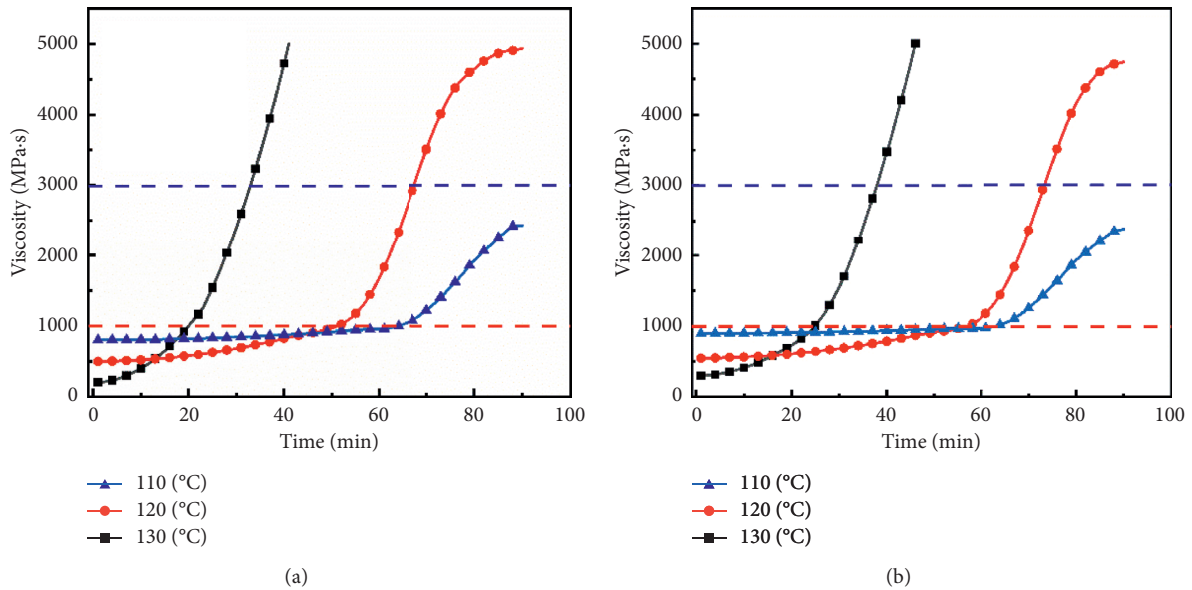


FIGURE 8: Viscosity-time curves of UA (a) and DA (b) at different curing temperatures.

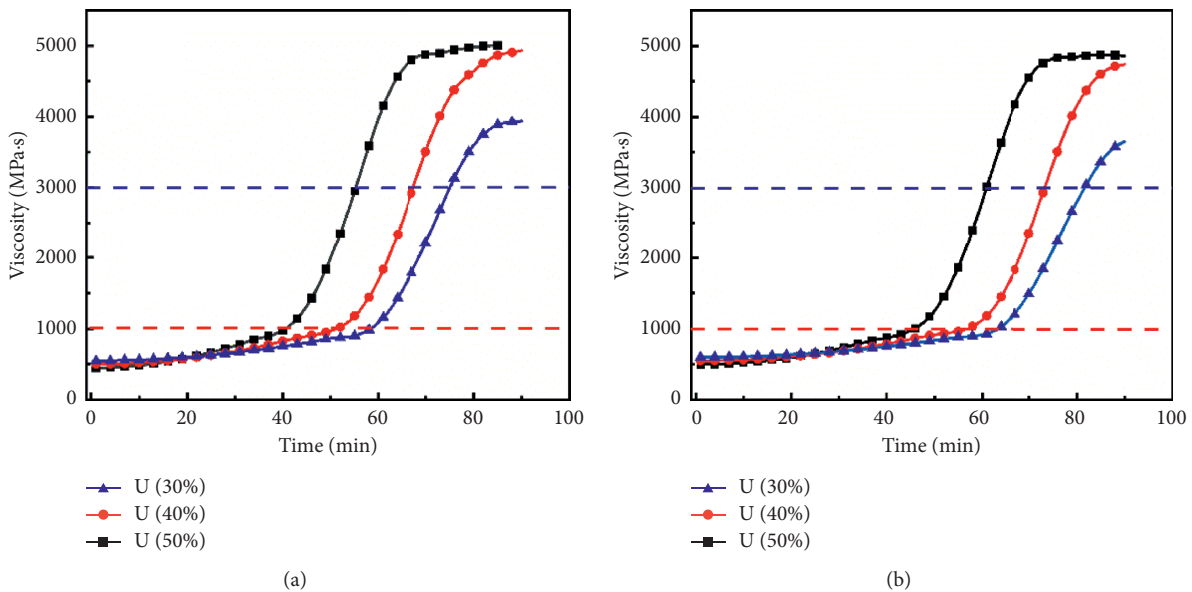


FIGURE 9: Viscosity-time curves of UA (a) and DA (b) with different ratios of epoxy resin to matrix asphalt binders.

4. Performance of ERMABs

In Section 3, the formula and preparation parameters of ERMABs are studied. Herein, the performance of UA and DA will be explored with the best ratio and test conditions and is compared with that of the control sample EA.

4.1. Phase Structure. In this section, phase structures of ERMABs are observed via a fluorescence microscope, as shown in Figure 12.

Figures 12(a)–12(c) are fluorescent photos of UA, in which the ratio of epoxy resin U to matrix binder is 30 to 70,

40 to 60, and 50 to 50 by weight, respectively. It is observed that as the proportion of epoxy resin increases, the matrix asphalt binder phase, the black part, gradually decreases, while the epoxy resin phase, the green part, gradually increases. When the ratio increases from 30:70 to 40:60, although the matrix asphalt binder phase is gradually decreasing, it is still the continuous phase, but when the ratio continues to increase to 50:50, the epoxy resin becomes the continuous phase and the matrix asphalt binder becomes dispersed phase. Therefore, 40:60 is the critical ratio for epoxy resin and matrix asphalt binder in the modified system, where the epoxy resin wraps the matrix asphalt binder and closes to the point of continuous phase reversal.

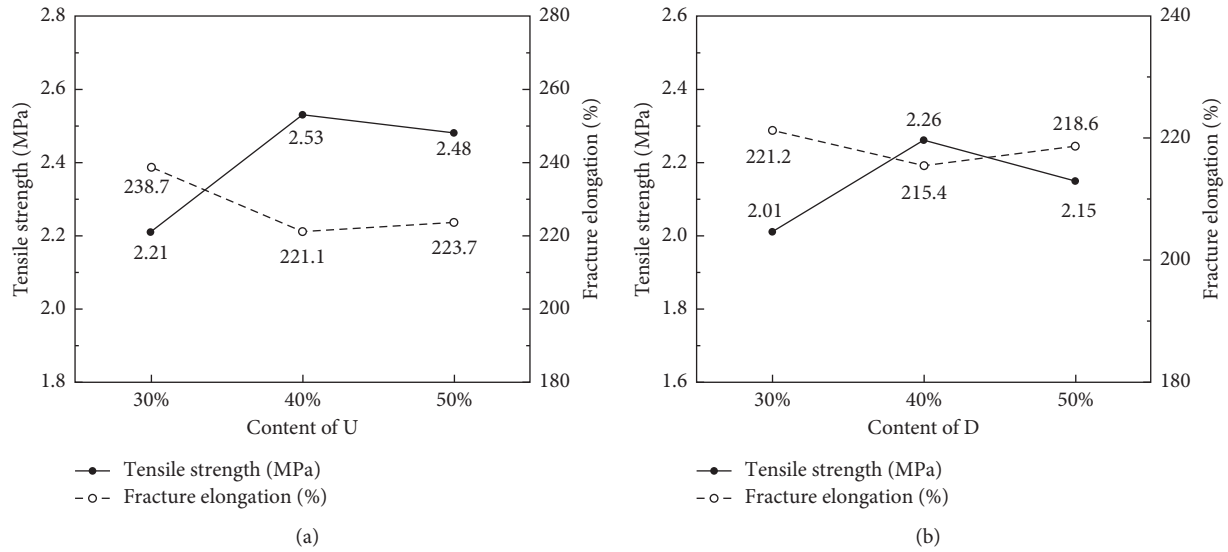


FIGURE 10: Tensile test results of UA (a) and DA (b) with different ratios of epoxy resin to matrix asphalt binders.

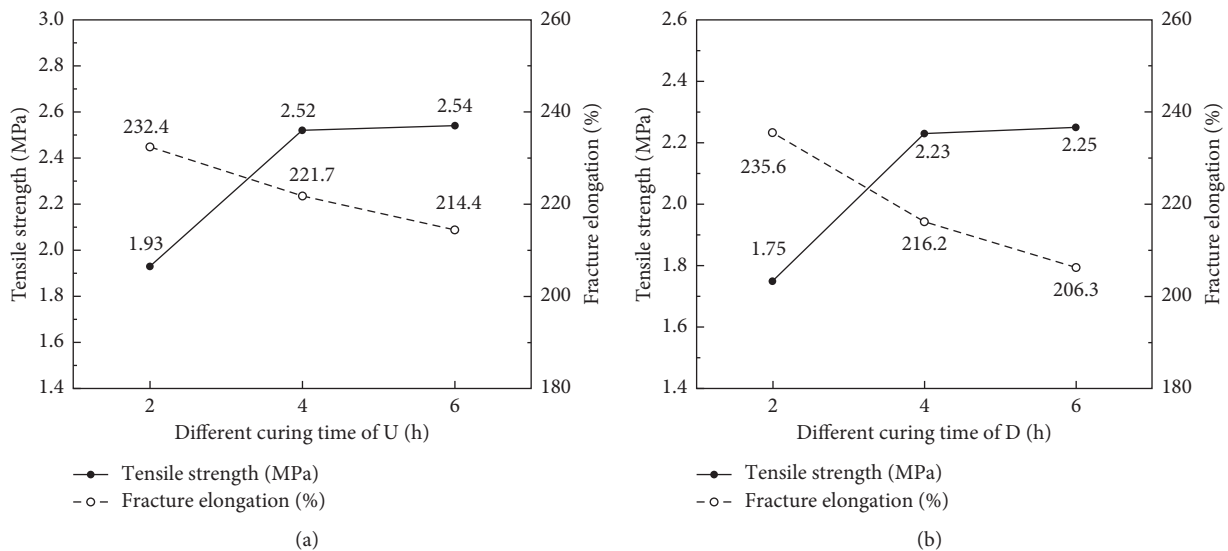


FIGURE 11: Tensile test results of UA (a) and DA (b) with different curing times.

Research studies on ERMABs show that when epoxy resin is used to modify the modified asphalt binder with this critical amount, it can play a more efficient role and contribute a tighter internal structure and better overall performance of the whole modified asphalt binders [26, 27]. Similar conclusions can be obtained from Figures 12(d), 12(e), and 12(f) of Figure 12.

Therefore, these photos of microscopic phase structures further verify the conclusion that the best ratio of epoxy resin to matrix asphalt binder in the modified system is 40 to 60.

4.2. TGA. TGA is an important method to study the thermal stability and composition of materials. In this section, TGA is used to study the differences in the thermal stability

among ERMABs when the ratio of epoxy resin to matrix asphalt binder is 40 : 60.

Figure 13 shows TG and DTG test results of three types of ERMABs. It can be seen that their thermal decomposition processes are similar, with three stages. At the first stage, from room temperature to 250°C, there is almost no thermal decomposition and mass loss is very small; thus, it is a thermally stable stage. The second stage, 250–550°C, is the thermal decomposition stage, where the ERMABs exhibit slow mass loss for the first time in the range of 220–340°C, caused by the volatilization of light-weight components of the ERMABs [28]. Then, there appears a sharp decline in thermal stability within the range of 340–450°C, which is mainly caused by the decomposition of macromolecules and epoxy resin network within asphalt binders [29, 30]. In addition, at this stage of rapid decline,

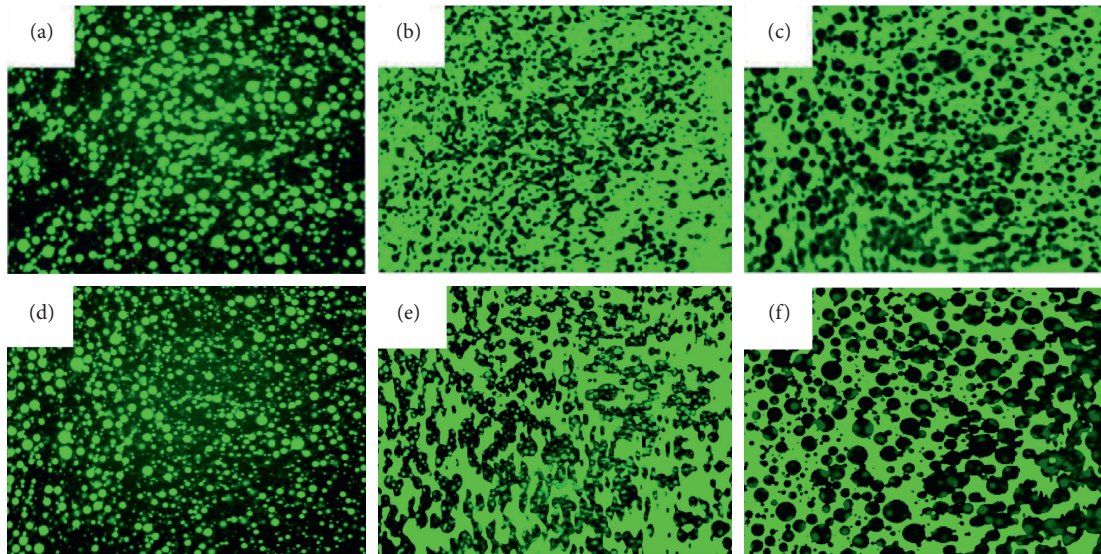


FIGURE 12: Fluorescent photos of binders with different dosages: (a) UA (30% U); (b) UA (40% U); (c) UA (50% U); (d) DA (30% D); (e) DA (40% D); (f) DA (50% D).

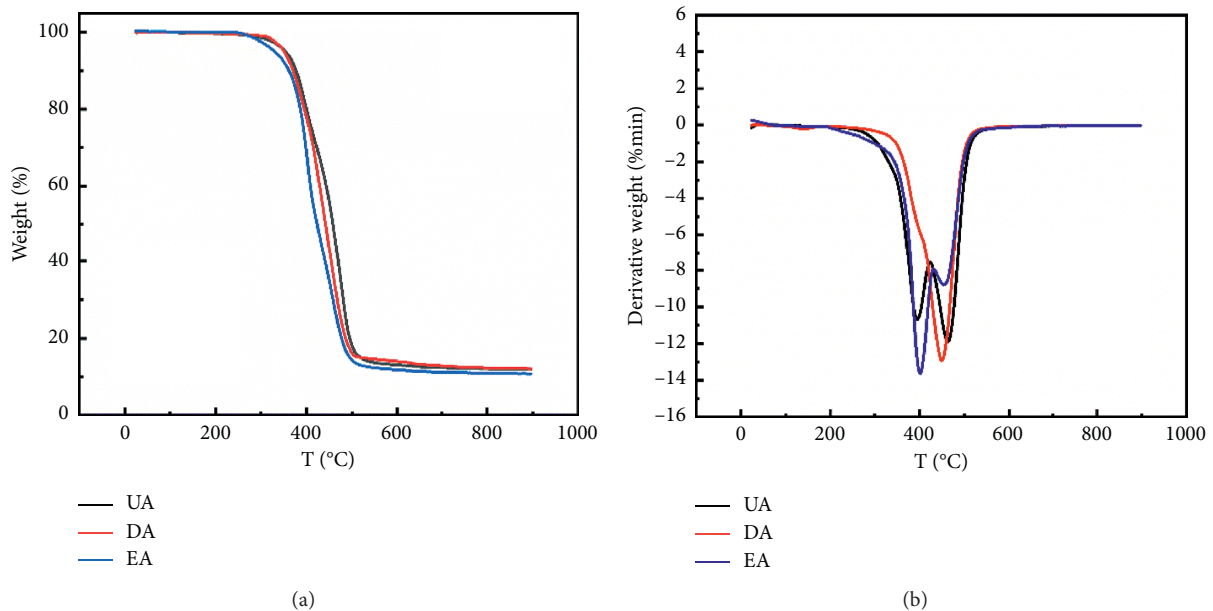


FIGURE 13: TG (a) and DTG (b) results of UA, DA, and EA.

the maximum decomposition temperature of EA is about 410°C, while that of UA and DA is about 450°C. The reason is that epoxy resins U and D are modified by polyurethane and dimer acid, respectively. In the third stage, when the temperature exceeds 550°C, the quality of the ERMABs basically remains unchanged. By calculating mass residue rates of ERMABs when the temperature is 800°C, it can be known that the mass residue rate of EA is 11.04%, while mass residue rate of the UA and DA is 13.21% and 13.76%, respectively.

Based on the above analyses, it is concluded that the thermal stability of EA is the worst, while the thermal stability of UA and DA shows little difference.

4.3. Low-Temperature Performance. Improving the low-temperature performance of ERMABs is one of the main purposes of this paper. Therefore, in this section, the low-temperature ductility test and low-temperature bending creep test are performed for the evaluation.

Figure 14 shows the low-temperature performance of three ERMABs. DA possesses the largest stretched length at either 5°C or 10°C, followed by UA and EA. This indicates that DA has the best low-temperature performance, followed by UA and EA. Furthermore, in terms of the degree of reduction, no matter at 5°C or 10°C, the tensile value of EA has a more significant drop compared with DA and UA. At 5°C, the stretch value of EA decreased by 38.5% and 29.4% compared with DA

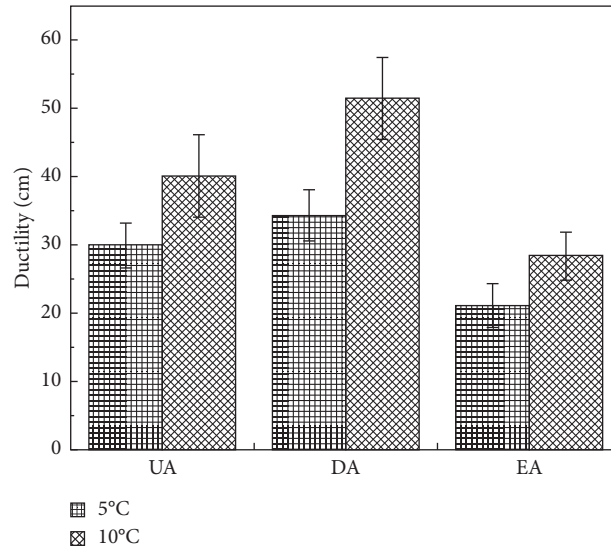


FIGURE 14: Ductility test results of UA, DA, and EA at 5°C and 10°C.

TABLE 2: BBR test results of UA, DA, and EA.

Types of binders	-6°C		-12°C		-18°C		-24°C	
	S (MPa)	m	S (MPa)	m	S (MPa)	m	S (MPa)	m
UA	95	0.443	177	0.349	282	0.311	526	0.209
DA	—	—	—	—	205	0.358	305	0.307
EA	201	0.366	298	0.297	497	0.253	—	—

and UA, respectively; at 10°C, the stretch value of EA decreased by 45.0% and 28.7% compared with DA and UA, respectively. This result indicates that the low-temperature performance of EA may be far worse than the other two modified asphalt binders prepared in this experiment.

Table 2 shows the creep stiffness modulus (S) and stress relaxation speed (m) of three types of ERMABs at different test temperatures. According to Table 2, as the temperature decreases, S increases rapidly and m decreases significantly, which means the low-temperature performance of the binders gets worse. SHRP research achievements reveal that the large creep stiffness modulus and the small relaxation speed make the pavement easy to crack at low temperatures. It is believed that the test binder could be used in the 10°C lower than the test temperature, where the S value of test binder is no larger than 300 MPa and m value is no smaller than 0.3 under the test procedure of ASTM D6373 [21]. According to this proposal, when the temperature is lower than -22°C, EA cannot be used, while UA and DA can still be used at -28°C. Moreover, the low-temperature limit of DA is even close to -34°C. These analyses reveal that the epoxy resin modified by polyurethane and dimer acid can greatly improve the low-temperature performance of the modified asphalt binders, showing the significance of the method on improving the low-temperature performance of modifiers.

The ductility and BBR test results both show that the modified asphalt binders by U and D could significantly improve the low-temperature performance of ERMAB.

4.4. Temperature Dependence. ERMAB still belongs to temperature-sensitive material dominated by asphalt binder, and its rheological properties would also change along with the test temperature. Figure 15 shows the complex moduli and phase angles of ERMABs within the temperature range of 30–90°C.

As the temperature increases, all the complex moduli decrease and phase angles increase, indicating that temperature increase will significantly reduce the deformation resistance of ERMABs. By comparing the test results of three types of ERMABs, the following conclusions can be drawn. First of all, EA, with the largest complex modulus and smallest phase angle, possesses the best resistance to deformation within the medium- and high-temperature ranges. Secondly, the complex modulus of UA is slightly lower than that of EA on the whole, but there is little difference between the two within the temperature range of 40–65°C. This shows that although the deformation resistance of UA is slightly lower than that of EA in the middle and high-temperature range, there is little difference in performance between the two in some certain temperature range. Thirdly, compared with the above two, DA has smaller complex modulus and larger phase angles. However, within the testing temperature range, the rate of decrease of its complex modulus is lower, making it finally closer to the complex moduli of EA and UA at relatively high-temperature stage. This indicates that DA has the worse temperature resistance to deformation in the testing temperature range, but its sensitivity to temperature changes is the lowest.

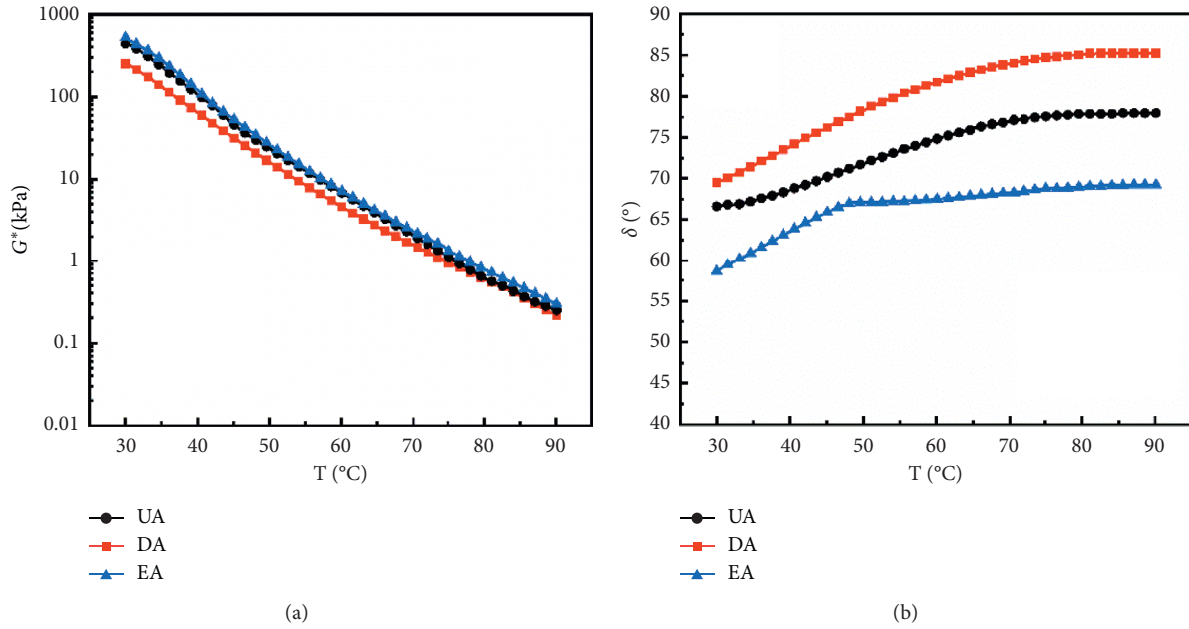


FIGURE 15: Complex moduli (a) and phase angles (b) of UA, DA, and EA.

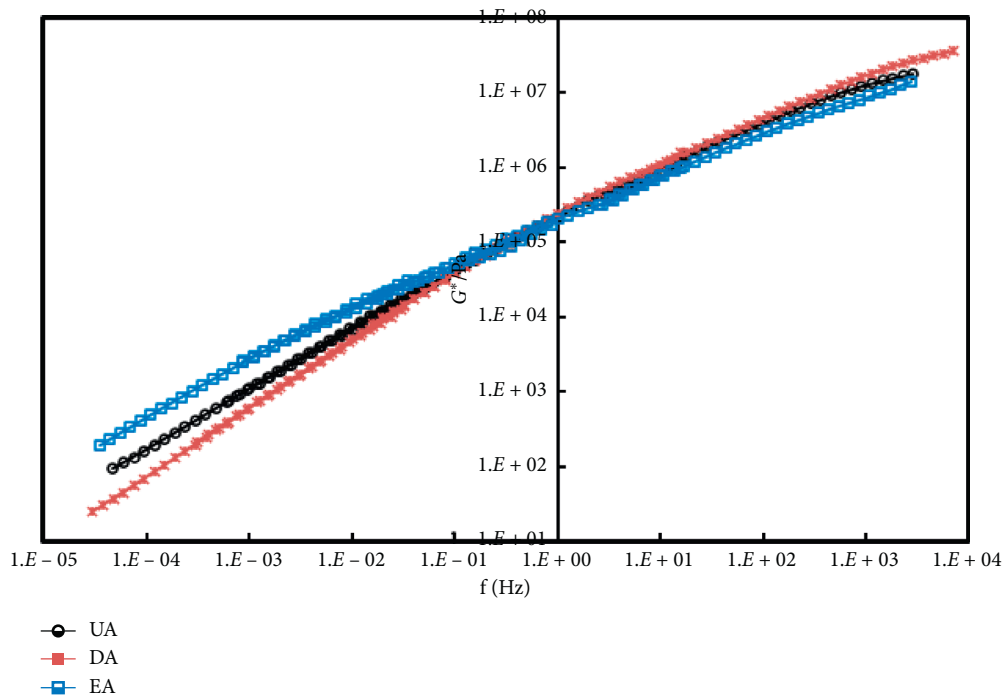


FIGURE 16: Complex modulus master curves of UA, DA, and EA.

In summary, EA still has a slight advantage in resisting temperature deformation within the medium- and high-temperature ranges, while DA has lower temperature sensitivity in the entire temperature range.

4.5. Frequency Dependence. In this section, the frequency sweep test is performed to study the frequency sensitivity of

the dynamic shear modulus of ERMABs within the range of linear viscoelasticity.

Figure 16 shows master curves of complex moduli of ERMABs. As the frequency increases, the complex moduli are significantly increased, showing a clear dependence on frequency. Specifically, in the low frequency (10^{-5} – 10^{-1} Hz), EA has the highest complex modulus, indicating that it possesses the best high-temperature stability. However, as

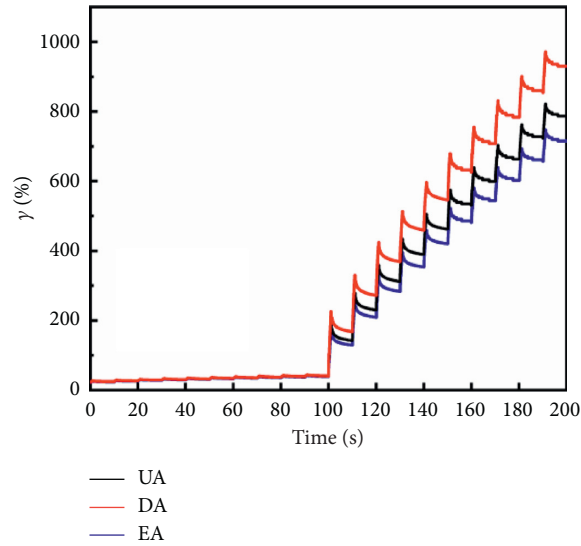


FIGURE 17: Results of shear strain-cycles of UA, DA, and EA in the MSCR test.

TABLE 3: Results of J_{nr} and R in the MSCR test.

		UA	DA	EA
R (%)	0.1 kPa	60.90	58.70	61.87
	3.2 kPa	34.04	32.21	36.83
$J_{nr} \times 10^{-3}$	0.1 kPa	20	26	17
	3.2 kPa	25	29	21

the frequency continues to increase, the growth rate of curve EA decreases and approaches to curves DA and UA within the medium frequency (10^{-1} – 10^1 Hz) and then gradually drops to be the lowest within the subsequent high frequency (10^1 – 10^4 Hz). This shows that there is little difference in the shearing resistance performance of the three at the medium temperature stage, while at the low-temperature stage, the cracking resistance performance of EA is the worst. This is consistent with the conclusion gained in the previous BBR test and temperature sweep test. Based on three frequency master curves, it can be seen that EA has the lowest dependence to frequency, followed by UA and DA.

4.6. Fatigue Performance. In this section, the fatigue performance of ERMABs is evaluated by MSCR. Figure 17 shows the cycle-strain test results. It can be known that three types of ERMABs show no obvious deformation when the shear stress is 0.1 kPa. However, once the shear stress increased to 3.2 kPa, all shear strain increased sharply, and significant cumulative deformation appears. Specifically, the shear strain and cumulative deformation of EA are the smallest, followed closely by UA, which gradually appears differences in shear strain and cumulative deformation along with the test cycles. In terms of DA, it emerges much larger shear strain and cumulative deformation since it is under the 3.2 kPa shearing stress, and the cumulative deformation is nearly 40% higher than that EA after the test. So, it can be known that DA has the worst fatigue performance.

Furthermore, the recovery rate (R) and nonrecoverable recovery creep compliance (J_{nr}) of ERMABs in the deformation are calculated and are shown in Table 3. It can be known that when the shear stress is 0.1 kPa, the deformation recovery rate and nonrecoverable creep compliance of all binders are very similar; while when the shear stress is 3.2 kPa, the deformation recovery rate of UA and DA is 92.4% and 87.5% of EA, and nonrecoverable creep compliance is 119.0% and 138.1% of EA, respectively. This result further illustrates that the fatigue resistance of UA and DA is worse than that of the control sample.

5. Conclusions

This paper tries to improve the low-temperature performance of ERMABs with not extended curing time. Three modified epoxy resins were prepared to modify the A-70 matrix asphalt binder. Then, the formula and prepared methods of ERMAB were optimized and determined. Moreover, a comparative analysis on the overall performance between two prepared ERMABs and the control sample were carried out. Main conclusions could be drawn as follows:

- (1) Polyurethane-modified epoxy resin or dimer acid-modified epoxy resin, with a suitable curing agent, can significantly improve the low-temperature performance of ERMAB, and the curing time meets the construction requirements. The optimal ratio of U to matrix asphalt binder to P is 40:60:4.4, and the optimal ratio of O to matrix asphalt binder to P is 40:60:1.9 by weight. The curing temperature is 120°C, and the curing time is 4 h.
- (2) When the ratio of epoxy resin to A-70 was 40:60, ERMAB witnesses the reversal of continuous phases and the best overall performance; thus, this ratio is appropriate.
- (3) The low-temperature performance of two ERMABs is significantly improved, and the application

temperature can even extend 18°C. Compared with the control sample, two ERMABs have almost the same rheological properties at medium temperature but slightly reduced high-temperature performance and fatigue resistance.

- (4) The epoxy resin asphalt binder modified by polyurethane possesses the best overall performance. Compared with the control sample, its low limit service temperature can extend 12°C, while its rheological property and fatigue resistance at medium- and high-temperature ranges show very little deterioration. Thus, it is an ideal and practical ERMAB with improved low-temperature performance.

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 no conflicts of interest.

Acknowledgments

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