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Experimental Study on the Micromorphology and Strength Formation Mechanism of Epoxy Asphalt During the Curing Reaction

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Featured Application: The evolution of the mechanical properties of epoxy asphalt during the curing process was analyzed to elucidate the mechanism responsible for the increase in the strength of epoxy asphalt, and the results can be used as a reference to achieve even mixing, curing, and time planning during epoxy asphalt pavement construction.

Abstract: The micromorphological changes and the strength formation mechanism of the curing of epoxy asphalt, which is mostly used for steel bridge deck pavements, were investigated. A tensile test was used to analyze the mechanical properties of epoxy asphalt, and Fourier transform infrared spectroscopy (FTIR) was used to determine the change in the epoxy peak area. Laser scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM) were used to observe two-dimensional and three-dimensional micromorphological changes, respectively, during the curing reaction of epoxy asphalt. The results of the tensile and FTIR tests on epoxy asphalt showed that the tensile strength and epoxy conversion rate both increased with the curing time and exhibited similar trends, indicating that the network formed by the crosslinking and polymerization of epoxy groups causes the increased strength of epoxy asphalt. The curing degree of epoxy asphalt during the curing reaction can be indirectly evaluated from the conversion rate of epoxy groups. The asphalt tended to evenly be dispersed in the continuous phase of the epoxy resin during the formation of the epoxy resin network, and the network structure increased the deformation of the epoxy resin. The epoxy asphalt curing reaction process was classified into three stages based on the degree of curing.

Keywords: epoxy asphalt; curing process; micromorphology; strength formation; Fourier transform infrared spectroscopy; mechanical properties; experimental study

1. Introduction

Heavy traffic or traffic overloading often leads to various types of distresses in asphalt pavement, such as cracks, rutting, and shoving [1–3]. To reduce asphalt pavement damage and adapt to various traffic and harsh environmental climate conditions, a variety of modified asphalts (e.g., polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA), and styrene-butadiene-styrene (SBS)) have been used to reduce rutting, shifting, cracking, and pitting on asphalt pavements and increase the pavement service life [4–7]. Although these polymers are beneficial for improving the high temperature stability, moisture resistance, and fatigue resistance of the asphalt mixture, these polymers do not change the thermoplasticity of the asphalt, and distresses such as rutting and cracking will still occur under high temperature and heavy load conditions [8].

A thermosetting epoxy asphalt is formed by adding epoxy resin and a curing agent to the asphalt. A crosslinking reaction between the epoxy resin and curing agent produces a three-dimensional network structure in the epoxy asphalt. The asphalt is dispersed in this crosslinked network and is constrained by the network structure, changing the thermoplasticity of the asphalt and producing a thermosetting material [9,10]. Compared with ordinary pavement, the pavement on orthotropic steel bridge decks experiences greater deformation and higher temperatures [11]. Ordinary modified asphalt mixtures have difficulty meeting the pavement requirements of orthotropic steel bridge decks under heavy traffic. Because modifiers (such as SBS, PE, and EVA) do not change the thermoplasticity of the asphalt, flow deformation occurs at high temperatures. Compared with thermoplastic modified asphalt, thermosetting epoxy asphalt has a higher strength and greater high-temperature stability, and it is widely used in orthotropic steel bridge deck paving [12–15].

Apostolidis et al. [16] evaluated the mechanical response of epoxy asphalt binders through numerical analysis. The results show that lower levels of activation energy increase the degree of hardening and the rate of viscosity development, and the polymerization rate of the epoxy asphalt binders is highly dependent on the temperature under various (non-) isothermal conditions. In addition, Apostolidis et al. [17] also studied the relationship between mechanical properties and heating conditions during the curing reaction of epoxy asphalt binders by establishing models and thermal analysis. The research results show that the strength increase associated with epoxy asphalt binders depends on heating conditions, and the rate of strength increase is faster at high temperatures. Yu et al. [18] prepared epoxy asphalt mixtures with different proportions of epoxy resin. Micromorphological studies on epoxy asphalt showed a phase transformation from a dispersed phase to a continuous phase for epoxy resin contents above 30%. The epoxy resin network that formed significantly increased the tensile strength and softening point of epoxy asphalt. Kang et al. [19] performed dynamic shear rheological tests (DSR) and dynamic mechanical thermal analysis tests (DMTA) to evaluate the rheological properties and thermal stability of epoxy asphalt, base asphalt, and SBS-modified asphalt. The excellent fatigue resistance and high-temperature stability of epoxy asphalt were attributed to a "two-phase" network that formed during the curing of epoxy asphalt. The epoxy resin network is the key factor in forming epoxy asphalt and differs fundamentally from other modified asphalt structures. Studying the curing process of epoxy asphalt and the formation of the epoxy network can elucidate the mechanism of strength formation of epoxy asphalt. Yu et al. [20] used Fourier transform infrared spectroscopy (FTIR) to analyze the curing process of epoxy asphalt. The curing rate remained unchanged during the initial curing stage and then decreased after 70 min. The results of a tensile test showed that the tensile strength increased slowly in the initial stage of curing and then increased rapidly, whereas the elongation at break decreased as the curing time increased. Cong et al. [21] used FTIR to investigate the curing process of epoxy asphalt and developed a curing reaction model that was in good agreement with experimental data. Tensile test results showed that as the curing time increased, the tensile strength increased and the elongation decreased. Morphological changes in the epoxy asphalt during the curing process were tracked under a fluorescence microscope and showed that the asphalt particle diameter increased with the curing time until a stable crosslinked structure formed.

Although changes in the viscosity, curing rate, and tensile properties of epoxy asphalt during the curing process have been reported, micromorphology research on epoxy asphalt during the curing reaction has mainly focused on phase transitions. In particular, there is a lack of quantitative analysis of the formation process of the epoxy resin crosslinked network structure and the relationship between the strength and the micromorphology of epoxy asphalt. The reaction stage characterization of epoxy asphalt needs investigation. Therefore, it is necessary to conduct an in-depth analysis of the microstructural changes in epoxy asphalt during curing to further understand the strength formation process and influential factors of epoxy asphalt.

Curing reactions occur during both the mixing and curing of hot mix epoxy asphalt, during which the microstructure and strength of the epoxy asphalt change gradually. Research on the microstructure

evolution and strength formation of hot mix epoxy asphalt during curing can help to elucidate the strength formation mechanism and optimize the design of epoxy asphalt, thereby serving as a reference for the construction process and curing control.

In this study, scanning electron microscopy (SEM) was used to observe the formation of the epoxy resin crosslinked network, to track spatial changes in the network microstructure, and to study epoxy asphalt etched off asphalt at different curing times. Laser scanning confocal microscopy (LSCM) was conducted to observe changes in the asphalt phase morphology of epoxy asphalt and micromorphological changes in epoxy asphalt during the curing process. In addition, changes in the characteristic peak areas of epoxy groups were tracked using FTIR, and changes in the conversion rate and the curing rate of epoxy groups during the curing reaction were quantitatively analyzed. The evolution of the mechanical properties of epoxy asphalt during the curing process was analyzed to elucidate the mechanism of the strength growth of epoxy asphalt.

2. Materials and Methods

2.1. Materials

Epoxy asphalt was prepared from a mixture of a base asphalt (A-70 petroleum asphalt (Shell (China) Co., Ltd., Foshan, Guangdong, China)) and an epoxy resin (Kindai Kasei Co., Ltd., Aichi-gun, Aichi-ken, Japan). The performance indexes of the base asphalt, the main agent, and the curing agent in the epoxy resin are shown in Tables 1–3 respectively.

Test Property	Technical Requirements	Test Results	Test Method
Penetration (25 °C, 100 g, 5 s, 0.1 mm)	60-80	62	ASTM D5
Softening point TR & B (°C)	≥47	50	ASTM D2398
Ductility (15 °C, 5 cm/min, cm)	≥100	> 100	ASTM D113
Density (15 °C, g/cm ³)	≥1.000	1.037	ASTM D1298
Solubility (%)	≥99.5	99.9	ASTM D2042
Flash point (°C)	≥260	319	ASTM D92

Table 1. Performance and technical requirements of A-70 base asphalt.

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Test Property	Technical Requirements	Test Results	Test Method
Viscosity (23 °C, Pa·s)	1000-5000	2130	ASTM D445
Specific gravity (23 °C)	1.00-1.20	1.137	ASTM D1475
Epoxide equivalent weight	190–210	207	ASTM D1652
Flash point (°C)	>230	244	ASTM D92
Appearance	Light yellow transparent liquid	Light yellow transparent liquid	Visual

Table 3. Performance and technical requirements of the curing agent for epoxy resin.

Test Property	Technical Requirements	Test Results	Test Method
Viscosity (23 °C, Pa·s)	100-800	234	ASTM D445
Specific gravity (23 °C)	0.80-1.00	0.864	ASTM D1475
Acid value (mgKOH/g)	150-200	153	ASTM D1652
Flash point (°C)	> 145	167	ASTM D92
Appearance	Light yellow brown liquid	Light yellow brown liquid	Visual

The epoxy asphalts were prepared using a high shear mixer (made by Bojin Chemical Machinery Co., Ltd., Hangzhou, China). According to the research [22], a ratio of 1:1 (asphalt-resin), which is commonly used in engineering applications, has a performance cost advantage. The epoxy resin was mixed with the curing agent before being added to the asphalt. The sample preparation process was as follows: the main agent (A) and the curing agent (B) of the epoxy resin were preheated to 60 °C, mixed at a 56:44 mass ratio, and stirred for three minutes. The resulting epoxy resin mixture and the base asphalt heated to 160 °C were gradually mixed at a 1:1 mass ratio at 160 °C while shearing and mixing under 1700 rpm rotation speed for four minutes to prepare the epoxy asphalt. Then, the molten epoxy asphalt was used to prepare test samples according to different test requirements. The preparation steps and storage and curing methods are listed in the different test methods below. Given the characteristics of the epoxy resin curing agent used, a curing temperature of 60 °C was used for the epoxy asphalt in this study. This temperature is generally used for standard curing in laboratory tests.

2.3. Tensile Test

Dumbbell-shaped test specimens were formed according to ASTM D638 standard and placed in a 60 °C oven to cure for a predetermined period of time. A tensile test was conducted to determine the tensile strength and elongation at break of the epoxy asphalt specimens at 23 °C using a universal testing machine (MTS, MTS Systems Co., Eden Prairie, MN., USA) at a tensile rate of 500 mm/min.

2.4. Fourier Transform Infrared Spectroscopy

The samples were prepared by coating epoxy asphalt onto a potassium bromide (KBr) thin plate and curing at 60 °C for different periods of time. The FTIR spectra were obtained using a VERTEX 70 (Bruker Co., Ettlingen, Baden-Wutenberg State, Germany) at a 4 cm^{-1} resolution.

2.5. Laser Scanning Confocal Microscopy

The process of preparing epoxy asphalt film samples is as follows. An iron wire was used to pick up the molten epoxy asphalt and drop it on a glass slide. The molten epoxy asphalt was then covered with a cover glass, which was pressed firmly to spread the epoxy asphalt evenly on the glass slide. The prepared slides were then put in an oven at 60 °C for different durations and observed. The morphological distribution of epoxy asphalt was observed and tracked using LSCM (Leica TCS SPE, Leica Microsystems Inc., Wetzlar, Germany) at 488 nm (Ar+ laser).

To quantitatively analyze the size and distribution of dispersed particles in the two-phase epoxy asphalt system, ImageJ (NIH, Bethesda, MD, USA) image analysis program was used. The average diameter (*D*n), weight average diameter (*D*w) and polydispersity index (PDI) of dispersed particles in the epoxy asphalt system were calculated according to a previous study [23] The lower the PDI value, the more uniform the particle diameter distribution.

2.6. Scanning Electron Microscopy

To observe the microscopic crosslinked network structure of epoxy resin, the fracture surface of the tensile specimen was soaked in toluene solution to remove the asphalt, and after etching the asphalt, the tensile specimen was placed at room temperature to dry. The specimen was then placed on an aluminum sheet and sprayed with gold to prepare the SEM sample. The micromorphology of epoxy asphalt was observed under a microscope (S3400N, Hitachi High Technologies Co., Tokyo, Japan) at 15 kV.

3. Results and Discussion

3.1. Mechanical Properties of Epoxy Asphalt During the Curing Process

To evaluate the changes in the tensile mechanical properties of epoxy asphalt during curing, tensile tests were performed on epoxy asphalt cured at 60 °C for different times, and the tensile strength and elongation at break were measured. The tensile strength and elongation at break of the epoxy asphalt specimens with different curing times are shown in Figure 1. In the early curing stage, the tensile strength in the epoxy resin was relatively low. As the curing time increased, the tensile strength of the epoxy asphalt increased rapidly. The rate of increase in the tensile strength decreased after 36 h, and the tensile strength stabilized at approximately 4 MPa after 72 h. The increase in epoxy asphalt strength may be related to the formation of an epoxy asphalt network structure, which is confirmed by the micromorphology characterization below. The reaction between the epoxy resin and the curing agent increases the cohesion of epoxy asphalt via the formation of a crosslinked network. It has been shown that the formation of a crosslinked epoxy asphalt network can reduce the elongation at break of epoxy asphalt [21]. The test results show that the elongation at break of epoxy asphalt decreased rapidly in the early curing stage. The rate of decrease in the elongation at break slowed down after 48 h, and the elongation at break stabilized at approximately 500% after 96 h. In summary, at the initial curing stage, the tensile strength of epoxy asphalt was relatively low, and the elongation at break was relatively high. As the curing reaction proceeded, the gradual formation of the crosslinked network was accompanied by an increase in the tensile strength and a gradual decrease in the elongation at break. After 96 h, the tensile strength and the elongation at break stabilized in conjunction with the formation of a relatively stable crosslinked epoxy asphalt structure.



Figure 1. Mechanical properties of epoxy asphalt with different curing times.

To compare the mechanical properties of the cured epoxy asphalt and the pure epoxy resin, tensile tests were conducted after curing at 60 °C for 96 h (by which time the two materials were completely cured). The test results are compared in Figure 2. Compared to that of pure epoxy resin, the tensile strength of fully cured epoxy asphalt was 27% lower, whereas the elongation at break was 79% higher. Thus, compared to the structure of pure epoxy resin, the three-dimensional (3D) network structure of epoxy asphalt resulted in a better deformation performance. This result is consistent with the findings of a previous report [23].



Figure 2. Comparison of the mechanical properties of fully cured epoxy asphalt and pure epoxy resin: (a) tensile strength and (b) elongation at break.

3.2. Quantitative Analysis of the Curing Process Using FTIR

The curing of epoxy asphalt was analyzed by using FTIR spectroscopy to track the change in the characteristic peak (915 cm⁻¹) of the epoxy group in epoxy asphalt at 60 °C with changes in the curing time [21]. FTIR tests were carried out on epoxy asphalt samples with different curing times. Figure 3 shows that the intensity of the epoxy group peak decreased as the curing time increased and stabilized after 69 h. The concentration of epoxy groups decreased as the curing time increased, reflecting the participation of the epoxy group in the curing reaction. Therefore, the curing process of epoxy asphalt can be quantitatively analyzed by tracking the change in the concentration of epoxy groups [20].



Figure 3. Local FTIR spectra of epoxy asphalt.

The two commonly used methods for FTIR quantitative analysis are peak height and peak area analyses. A vertical line is drawn between the peak vertex and the horizontal axis. The peak height is the distance between the vertex and the intersection of the vertical line and the baseline. The area enclosed by the curve of the absorbance peak and the baseline is the peak area. Peak area analysis was used in this study. To eliminate the influence of the coating thickness of the infrared samples on the absorbance peak area, an internal standard method was used to determine the variation in the concentration of characteristic groups with the curing time. The characteristic peak of a group that does not participate in the curing reaction (the benzene ring group at 830 cm⁻¹) was selected as a reference peak. The ratio of the peak area of the epoxy group (915 cm⁻¹) to that of the benzene ring group (830 cm⁻¹), A_{915}/A_{830} , was used to represent the variation in the epoxy group concentration [24]. FTIR was used to quantitatively analyze the epoxy group concentration at different curing times, and then the conversion rate of epoxy group with curing time was calculated based on the epoxy group concentration to indirectly evaluate the curing degree of epoxy asphalt. The conversion rate (α) of the epoxy groups in the curing reaction was calculated as follows:

$$\alpha = 1 - \frac{(A'_{915}/A'_{830})_t}{(A_{915}/A_{830})_0} \tag{1}$$

where $(A'_{915}/A'_{830})_t$ and $(A_{915}/A_{830})_0$ denote the aforementioned area ratio at curing times of *t* and before the start of the curing reaction, respectively.

To accurately obtain the area of the absorbance peak of the chemical functional group, Peakfit (v4.12, Systat Software Inc, San Jose, CA, USA) was used in this study to fit the FTIR sample spectra [25]. The Peakfit software performed a baseline calibration on the selected wavenumber region and then initially fitted the approximate position and number of peaks based on the first derivative of each spectral line. Multiple fittings were achieved using Gaussian peaks. After the residual was minimized, the absorbance peak area of the subpeak was quantitatively obtained. The fitting results of the absorbance peaks are shown in Figure 4.



Figure 4. Schematic of the fitting results of the characteristic absorbance peak area: (**a**) wavenumber 915 cm⁻¹ and (**b**) wavenumber 830 cm⁻¹.

The value of α at each curing time was calculated using Equation (1). The curing reaction degree of epoxy asphalt, G_{α} , was defined as follows:

$$G_{\alpha} = \frac{\alpha_t}{\alpha_{144}} \times 100\% \tag{2}$$

where α_t is the conversion rate of epoxy groups at a curing time t, and α_{144} is the corresponding final stable conversion rate at a curing time of 144 h.

The calculated α and G_{α} values are shown in Table 4. It can be seen that α increased with time: at 69 h, α reached 0.504, and the curing reaction degree exceeded 90%; α eventually stabilized at 0.55.

Curing Time / h	$(A'_{915}/A'_{830})_t$	$\frac{(A^{'}_{915}/A^{'}_{830})_{t}}{(A_{915}/A_{830})_{0}}$	Conversion Rate of Epoxy Groups, α	Curing Reaction Degree, G_{α} / %
0	0.109	1.000	0.000	0
3	0.104	0.958	0.042	8
7	0.100	0.915	0.085	15
22	0.083	0.759	0.241	44
29	0.085	0.782	0.318	58
40	0.067	0.615	0.385	70
46	0.065	0.592	0.408	74
69	0.054	0.496	0.504	91
93	0.050	0.456	0.544	98
120	0.049	0.451	0.549	99
144	0.049	0.448	0.552	100

Table 4. Calculated conversion rate of epoxy groups, α , and the curing reaction degree of epoxy asphalt, G_{α} .

To correlate α with the tensile strength of epoxy asphalt, $G\alpha$ was compared to the curing degree of epoxy asphalt as represented by the tensile strength, G_s :

$$G_S = \frac{S_t}{S_{120}} \times 100\%$$
(3)

where S_t and S_{120} are the tensile strengths of epoxy asphalt at curing times *t* and 120 h, respectively, where S_{120} is considered the ultimate stable tensile strength. The results for G_{α} and G_s are compared in Figure 5. Figure 5a shows similar increasing trends for G_{α} and G_s , indicating that the strength of epoxy asphalt is mainly derived from the epoxy resin crosslinked network. Since there is no direct correspondence between α and the curing time for the development of the tensile strength, polynomial regression was used to fit G_{α} , as shown in Figure 5b, and to obtain G_{α} values at 12, 24, 36, 48, 72, 96, and 120 h (Table 5). A correlation analysis was conducted on G_s and G_{α} . The results in Figure 5c show that G_{α} and G_s are linearly correlated, with an R^2 greater than 0.99, indicating that G_{α} and G_s are highly correlated. Thus, α can be used to indirectly evaluate the tensile strength and curing degree of epoxy resin.



Figure 5. Comparison of curing degrees as represented by the tensile strength and conversion rate of epoxy groups: (**a**) increase curves for both curing degrees; (**b**) polynomial fitting curve for conversion rate of epoxy groups, and (**c**) correlation curve between two curing degrees.

Table 5. Curing degrees at different curing times as characterized by the epoxy group conversion rate and tensile strength.

Curing Time/h	12	24	36	48	72	96	120
G_{α} /%	27	48	65	77	93	99	99
G_s /%	17	39	64	76	97	99	100

3.3. Morphological Analysis

The curing of epoxy asphalt was further analyzed by tracking the micromorphological changes of epoxy asphalt with different curing times using LSCM. Fluorescence images of the epoxy asphalt samples cured at 60 °C for different times are shown in Figure 6. The fluorescent and dark phases correspond to the epoxy resin and the base asphalt, respectively. The epoxy resin, the curing agent, and asphalt were mixed and then stirred by shearing to evenly disperse the three components, as shown in Figure 6a. After mixing, the epoxy resin and the curing agent underwent a polymerization reaction, where the homogeneous phase of asphalt microparticles was polymerized into larger particles to form a two-phase system with an island-like structure, with asphalt as the dispersed phase and epoxy resin as the continuous phase, as shown in Figure 6b–e. As the curing reaction proceeded (Figure 6e–h), an epoxy resin crosslinked network gradually formed. The crosslinking density then continuously increased, and the large asphalt particles were gradually divided into small particles by the epoxy resin network. At 72 h, the asphalt particle diameter gradually stabilized at an average particle diameter of approximately 20 μ m (Figure 6h,i). The particles were evenly dispersed in the epoxy resin, forming a stable two-phase 3D network structure. This result is consistent with that observed by Liu et al. [26],

that is, the diameter of asphalt particles first increases and then decreases during the epoxy asphalt curing process.



Figure 6. LSCM photographs of epoxy asphalt samples with different curing times (60 °C): (**a**) 0 h, (**b**) 0.5 h, (**c**) 3 h, (**d**) 5 h, (**e**) 12 h, (**f**) 24 h, (**g**) 48 h, (**h**) 72 h, and (**i**) 96 h.

Two definitions are introduced to quantify the dispersion of asphalt particles in the epoxy resin crosslinked network: homogeneity (also known as overall uniformity) and dispersion. Homogeneity refers to the amplitude of concentration fluctuations of the dispersed phase, and dispersion refers to the size distribution range of the particulate phase. The image analysis program ImageJ was used to determine and statistically analyze the asphalt particle sizes in epoxy asphalt [27]. Figure 7 shows the asphalt particle size distribution in epoxy resin for different curing times. In the initial curing stage, the distribution range of the asphalt particle diameters increased from 0–50 μ m to 0–100 μ m. After 12 h, the particle size distribution range gradually decreased and returned to a stable normal distribution in the 0–40 μ m range at 96 h. As the curing reaction proceeded, the diameter distribution changed from narrow to wide, then retracted, and stabilized at 0–40 μ m, indicating that the asphalt particles tended to become evenly distributed in the epoxy resin as the curing time increased.



Figure 7. Diameter distribution of asphalt particles for different curing times.

According to Liu et al. [23], the changes in the dispersity of the asphalt particles with the curing time were determined by calculating D_n , D_w , and *PDI* of the asphalt particles using the following equations:

$$D_n = \frac{\sum n_i D_i}{\sum n_i} \tag{4}$$

$$D_w = \frac{\sum n_i D_i^2}{\sum n_i D_i} \tag{5}$$

$$PDI = \frac{D_w}{D_n} \tag{6}$$

where n_i is the number of particles with a diameter D_i . The values of D_n , D_w , and PDI of the asphalt particles for different curing times are given in Table 6. In the initial curing stage, D_n of the asphalt particles increased with the curing reaction time. After 12 h, D_n gradually decreased and stabilized at approximately 18 µm. The *PDI* first increased and then decreased, indicating relatively low uniformity of the epoxy asphalt dispersion in the initial curing stage. The formation of the crosslinked network resulted in the gradual division of large asphalt particles into small particles, increasing the dispersion uniformity.

Sample	D_n (μ m)	D_w (μ m)	PDI
0.5 h	14.5	19.6	1.35
3 h	15.9	21.8	1.37
5 h	19.2	27.0	1.40
12 h	19.5	33.2	1.70
24 h	18.0	29.1	1.62
48 h	17.5	26.6	1.52
72 h	18.1	20.8	1.15
96 h	18.0	20.7	1.15
96 h	18.0	20.7	1.15

Table 6. D_n , D_w , and *PDI* of asphalt particles for different curing times.

The evolution of the microscopic structural characteristics of the 3D epoxy resin crosslinked network during the curing process was investigated by performing SEM on epoxy asphalt samples (after asphalt etching) with different curing times. Figure 8 shows the SEM images of the epoxy resin for different curing times (12 h, 24 h, 36 h, 48 h, 72 h, and 96 h) at 300x magnification. The etched epoxy asphalt contained many pores of various sizes, indicating that the asphalt was wrapped by the epoxy resin network and that the epoxy resin network was filled with asphalt. As shown in Figure 8a, the crosslinked epoxy asphalt network did not form before 12 h. The crosslinked network gradually formed after 24 h, as shown in Figure 8b. The remaining pores had irregular shapes. In the earlier LSCM images, the pores were approximately round, showing that the pore shape depends on the curing degree of the epoxy resin. At the early curing stage, the epoxy resin had a low degree of crosslinking and was relatively soft; the sample pores after etching were large and deformed into irregular shapes at room temperature during drying. After 36 h (when α reached approximately 0.36), the crosslink density of epoxy resin continuously increased, the pores became smaller and denser, and the epoxy resin formed a relatively stable and compact 3D network skeleton (Figure 8c-f), in agreement with the LSCM images. These phenomena reflect that in the early curing stage, the initially epoxy resin network was weak and easily deformable. As the curing reaction proceeded, the continuous increase in the crosslink density of the epoxy resin strengthened the 3D network structure, while also lowering the ductility of the epoxy asphalt. These results are consistent with the continuous increase in the tensile strength and the decrease in the elongation at break of the epoxy asphalt with increasing curing time.



Figure 8. SEM images of epoxy resin with different curing times (60 °C): (**a**) 12 h, (**b**) 24 h, (**c**) 36 h, (**d**) 48 h, (**e**) 72 h, and (**f**) 96 h.

A microscopic morphology analysis showed that the epoxy asphalt curing process is dominated by the reaction of the epoxy resin oligomer. In this process, heterogeneous microgels are first generated in the system, then gradually form large gels (Figure 8a), and finally form a gel-like polymer (Figure 8b). As the reaction continues, the crosslink density continuously increases, forming a highly crosslinked polymer with a 3D network structure, as shown in Figure 8f. From a molecular chemistry perspective, the epoxy asphalt curing process is essentially the polymerization of epoxy monomers into single chains that are repolymerized into a crosslinked network, which gradually densifies [28,29]. During the curing reaction of epoxy asphalt, the epoxy monomers are polymerized into single chains, and the single chains are repolymerized into crosslinked network. The molecular weight of the epoxy resin continuously increases, and the compatibility between the epoxy resin and the thermoplastic asphalt decreases, which promotes phased development. The dispersed asphalt particles are surrounded by a crosslinked network of epoxy resin, forming a two-phase 3D network with each other. A schematic of this process is shown in Figure 9. The results of the micromorphological changes that are shown in Figures 7 and 8 are consistent with this process.



Figure 9. Schematic of the epoxy asphalt curing process.

In summary, an analysis of the test data shows that the main mechanism of epoxy asphalt strength formation is the curing of epoxy asphalt into a stable 3D network. The curing process can be divided into three stages: an initial stage, an intermediate stage, and a late stage. In the initial stage, G_{α} is less than 27%, no network exists, the reactivity is high, and the material strength increases rapidly. In the intermediate stage, G_{α} is between 27% and 65%, a 3D network starts to form, and the network skeleton is relatively soft and easy to deform. Thus, the epoxy asphalt should not be disturbed to avoid affecting the increase in the epoxy resin strength. In the late stage, G_{α} is greater than 65%, and the skeleton gradually densifies into a stable two-phase 3D crosslinked epoxy resin network containing asphalt particles. This dense uniform 3D network in the cured epoxy asphalt increases the deformation of the epoxy resin. The asphalt fills in and protects the epoxy resin against aging, and the crosslinked network formed by the polymerization of the epoxy resin changes the thermoplasticity of the asphalt, resulting in a high strength and good thermosetting properties.

4. Conclusions

The conclusions below were drawn from an experimental study on the microstructural changes and the strength formation mechanism during the curing process of epoxy asphalt.

(1) The epoxy group content was quantitatively determined using FTIR and combined with the results for the tensile mechanical properties of epoxy asphalt. The conversion rate of epoxy groups is significantly related to the tensile strength of epoxy asphalt. The curing strength of epoxy asphalt increases via the development of a 3D network of crosslinked epoxy resin. The curing degree of epoxy asphalt can be evaluated using the conversion rate of epoxy groups.

- (2) A morphological analysis shows that during the curing process of epoxy asphalt, the asphalt PDI first increases, then decreases, and eventually stabilizes at approximately 1.15. The polymerization of epoxy resin into a spatial network results in a gradual two-phase separation, whereby asphalt is evenly distributed in a 3D epoxy resin network. The elongation at break of the cured epoxy asphalt is approximately 80% higher than that of the pure epoxy resin. The 3D network of epoxy asphalt increases the deformation of the pure epoxy resin.
- (3) In the curing of epoxy asphalt, epoxy resin is crosslinked into a stable 3D network structure in three stages: an initial stage (G_{α} less than approximately 27%), an intermediate stage (G_{α} between approximately 27% and 65%), and a late stage (G_{α} greater than approximately 65%).
- (4) In engineering practice, during the mixing, transporting, paving, and rolling process, the epoxy asphalt mixture is in the initial stage of curing and has a high reactivity. In the intermediate and late stages of curing, epoxy asphalt concrete should not be disturbed to avoid affecting the strength increase and long-term pavement performance. Attention should also be given to shortening the construction interval between the upper and lower pavement layers, completing the overall construction to the greatest extent possible in the initial stage of curing, and reducing disturbances to the concrete in the lower pavement layer.

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