

Laboratory Investigation of the Properties of Asphalt Modified with Epoxy Resin

Jianning Yu,¹ Peiliang Cong,^{1,2} Shaopeng Wu¹

¹Key Laboratory of Silicate Materials Science and Engineering, Ministry of Education, Wuhan University of Technology, Wuhan 430070, China

²School of Materials Science and Engineering, Chang'an University, Xian 710064, China

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ABSTRACT: Epoxy asphalts were prepared by mixing styrene-butadiene-styrene (SBS) modified asphalt with epoxy resin. The curing process and morphology of epoxy asphalts were characterized by infrared spectroscopy and fluorescent microscope, respectively. The effects of epoxy resin contents, ratio of curing agent to epoxy resin and curing temperature on properties of epoxy asphalt were investigated. Results indicated that epoxy resin and epoxy asphalt showed similar curing efficiency. Epoxy asphalts can be cured at 120 or 60°C and its viscosity at 120°C can meet the demands of asphalt mixture mixing and paving. The chemical reaction of epoxy resin in epoxy asphalt is slow and reaction occurs not only with the curing agent but also carboxylic acid in epoxy asphalt.

The microstructure of epoxy asphalt transforms from the dispersed structure to networks structure with epoxy resin content increasing and phase transition starts when 30 wt % epoxy resin present in asphalt. The softening point and tensile strength of epoxy asphalt increased with epoxy resin contents increasing. The softening point and tensile strength of epoxy asphalt were markedly improved when epoxy resin content was more than 30 wt %, which is attributed to formation of continuous structure of epoxy resin. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3557–3563, 2009

Key words: epoxy resin; modified asphalt; FTIR; morphology; mechanical properties

INTRODUCTION

Asphalt has been widely used in paving industry. However, asphalts are brittle and hard in cold environments and soft in hot environments. In addition, there are many types of failures, such as the low-temperature cracking, fatigue cracking, and the rutting (or permanent deformation) at high temperature, that can reduce the quality and performance of road pavement during “in life” service. Any improvement in service life is a great economical advantage. The modification of asphalt is an attempt to extend the service life and improve the performance of asphalt pavements.¹ Polymers have been widely used to improving properties of asphalt. Asphalt for paving is modified with polymers to improve rut resistance, fatigue resistance, cracking resistance, and stripping resistance resulting from increases in asphalt elasticity and stiffness.^{2–4} Generally, plastomeric polymers can improve rut resistance, but they are inferior to elastomers due to lack of significant improvements in fatigue resistance and cracking resistance.^{5–8} In addition, plastomeric polymers cannot improve low-temperature performance

of asphalt. Elastomers can improve fatigue resistance and cracking resistance, but it is limited to improve heat resistance.

Orthotropic steel decks have been widely applied to long span bridges because its light weight contributes to reduce dead load. Compared with the general pavement, the paving layer on the deck endure larger deform and higher temperature. So, some polymers were used to prepare modified asphalt concrete for steel bridge deck paving. However, plastomeric or elastomers polymers modified asphalt cannot change the thermoplastic nature of asphalt, which means that asphalt mixture flow easily at high temperature.^{9–15} To resolve this problem, researchers have been trying to find more efficient modifiers to improve the performance of asphalt mixture. In the research process, asphalt binders and epoxy resin are used in combination for resolving the afore-mentioned problems.^{16–20} Epoxy asphalt is prepared by mixing an epoxy resin and an asphalt material in the presence of a curing agent.^{21–23} But there is little published data on epoxy asphalt binder's preparation and properties of epoxy asphalt.^{24–26}

In this article, epoxy asphalts were prepared by mixing styrene-butadiene-styrene (SBS) modified asphalt with different amounts of epoxy resin. SBS was used to improve the ductility of epoxy asphalt. The function group change of epoxy asphalt during

Correspondence to: J. Yu (jianningyu@163.com).

TABLE I
Physical Properties of Asphalt

Physical properties	Measured values
Penetration (25°C, 0.1 mm)	77
Softening point (°C)	45.9
Ductility (15°C, cm)	118
Ductility (5°C, cm)	13.4
Viscosity (135°C, mPa s)	500

curing was characterized by Infrared Spectroscopy and the morphology of epoxy asphalt was observed by fluorescent microscopy. The effects of curing temperature, curing time, and epoxy resin content on the properties of epoxy asphalt were investigated.

EXPERIMENTAL

Raw materials

The 60/80 pen grade asphalt was used, and the physical properties of the asphalt are listed in Table I. The SBS used, Grade 1301, was produced by the Yueyang Petrochemical Co., Ltd., China. This was a linear-like SBS, containing 30 wt % styrenes, and the average molecular weight of SBS is 120,000. The epoxy resin used was diglycidyl ether of bisphenol A and its epoxy value is 0.52 mol/100 g. It was made in Shanghai Xinhua Resin Co., Ltd., Shanghai, China. Methyl tetrahydro phthalic anhydride (MTHPA) curing agent was provided by Jiaying Fine Chemical Co., Ltd., Zhejiang province, China. All materials were commercially available and used as received.

The chemical structure of the epoxy resin and the curing agent used appear in Figure 1.

Methods

Asphalt was heated to 170°C ± 5°C in an oil-bath heating container until it flowed fully. The 3 wt %

SBS was mixed into the asphalt under 5000 rpm rotation speed about 60 min to ensure the blend became essentially homogenous. When the temperature of the SBS/asphalt blend was reduced to 120°C, the appropriate amounts of curing agent (the ratio of curing agent to epoxy resin was 7.5 : 10 by mass) were added into the blend and mixed for 30 min with a lab mixer set fast enough (usually 500 rpm) to create a small vortex, without whipping excessive air into the sample. The epoxy asphalt was obtained when the desired amount of epoxy resin (preheat to 120°C) was added into the blend and the mixer continued to stir the blend for 5 min under the same mixing condition. Then the sample for test was prepared and cooled in refrigerator about 30 min at zero temperature. Epoxy asphalts with 10, 20, 30, 40, and 50 wt % epoxy resin (including curing agent) were prepared, respectively.

The effect of curing temperature and time on property of epoxy asphalt was assessed by softening point in accordance with ASTM D36. The curing conditions are as following: (1) the sample was test directly when it was prepared, (2) the sample was test after different curing time at 120°C, and (3) the sample was test after different curing time at 60°C. For this assessment, the samples of each sample were mold before curing.

Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was used to measure the viscosity of epoxy asphalt referring to ASTM D4402. The appropriate amounts of epoxy asphalt immediately poured into the sample chamber and immediately placed in the thermo container to decrease the reaction between epoxy resin and curing agents, and then the spindle was lowered into the chamber that have been preheated to 120°C to test the viscosity.

The morphology of epoxy asphalt was observed using a fluorescent microscope (Model YS100, Yuyangfeng Co., China) at room temperature. Squashed slides of epoxy asphalts were prepared

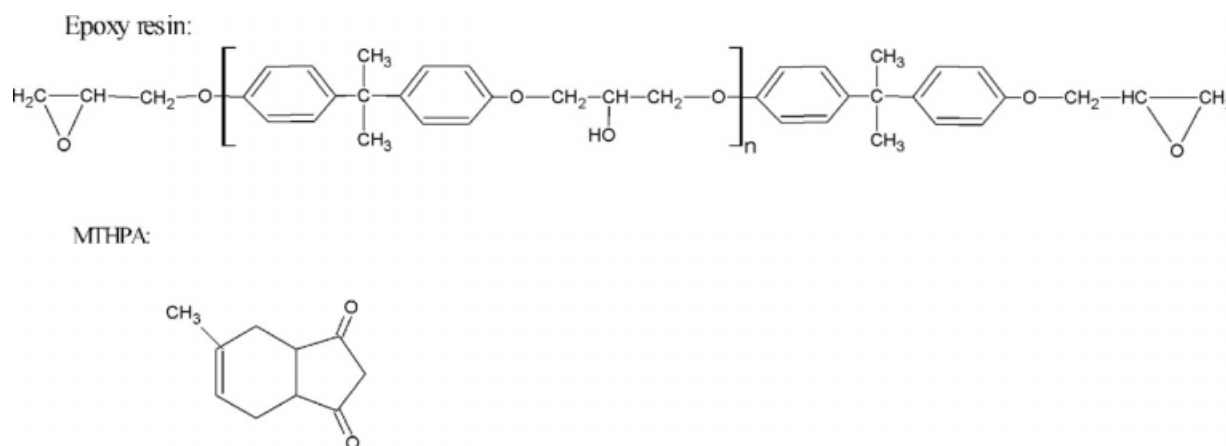


Figure 1 The molecular structure of epoxy resin and acid anhydride used.

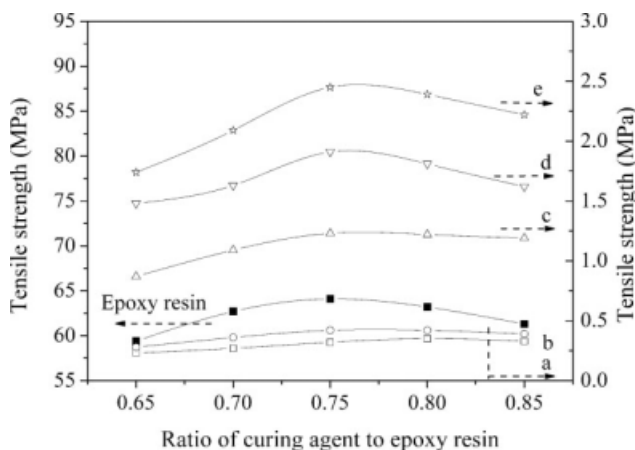


Figure 2 Effect of the ratio of curing agent to epoxy resin on tensile strength of epoxy resin and epoxy asphalt containing epoxy resin: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, (e) 50 wt %.

using very small amounts of the heated sample and viewed under the microscope at a magnification of 400 at ambient temperature.

Fourier transform infrared (FTIR) Spectroscopy (NEXUS, Thermo Nicolet, USA) was used to obtain the IR spectra of epoxy asphalt. Sample was prepared by casting film onto a potassium bromide (KBr) thin plate, and the spectra were obtained by 4 cm⁻¹ resolution. The sample was placed in thermo container in FTIR spectroscopy and increases the temperature of sample to 120°C and stays at constant temperature about 5 min. Then the test was taken at 120°C and the peak areas of relevant wave numbers were calculated over wave numbers ranging at different time. The interval, from mixing epoxy asphalt and curing agent to obtaining the first IR peak spectra, took approximately 15 min.

The tensile strength and elongation at break of epoxy asphalt was test on Electro-Hydraulic Servocontrolled Testing System (Model Instron 1341, Instron Ltd. UK) referring to ASTM D638 at ambient temperature. The strain rate was 500 mm/min.

RESULTS AND DISCUSSION

Effect of asphalt on curing of epoxy resin

Figure 2 shows the effect of the ratio of curing agent to epoxy resin on tensile strength of epoxy resin and epoxy asphalt. The tensile strength of epoxy resin increase with the ratio of curing agent to epoxy resin increasing when ratio is lower than 0.75. When ratio of curing agent to epoxy resin is 0.75, the tensile strength is 64.1 MPa. But the tensile strength decrease with the ratio when ratio is more than 0.75. Thus, the 0.75 is optimum ratio of curing agent to epoxy resin. The relationship of tensile strength of epoxy asphalt with different epoxy resin and the ra-

tio of curing agent to epoxy resin showed similar trends. But, the 0.8 is optimum ratio of curing agent to epoxy resin when epoxy resin contents lower than 20 wt %. The optimum ratio trends to 0.75 with the epoxy resin contents increasing, and epoxy asphalt with 40 wt % and 50 wt % epoxy resin showed high-tensile strength when the ratio of curing agent to epoxy resin is 0.75. Therefore, compared with epoxy resin, asphalt has a little effect on curing of epoxy resin in epoxy asphalt.

Effect of curing temperature and time

Figure 3 presents the change of softening points of the epoxy asphalts containing different concentration of epoxy resin with curing time at 120°C. The softening point of the mix of epoxy resin modified asphalt is lower than asphalt's and the more epoxy resin content, the lower softening point at zero curing time. When the concentration of epoxy resin was 0 wt % and 10 wt %, the softening point was 45.9°C and 46.1°C, respectively. It was 34.6°C as 50 wt % epoxy resin added. It is because the viscosity of uncured epoxy resin is lower than that of asphalt. But the softening point of epoxy asphalt increased with the curing time increase after curing began. The softening point was 61.4°C for 10 wt % epoxy resin modified asphalt and it was 92.3°C for 50 wt % epoxy resin modified asphalt when curing time was 60 min. Figure 4 shows the change of softening points of the epoxy asphalts with curing time at 60°C. Epoxy asphalt should be paved before cured completely. Therefore, it is important to investigate the performance of epoxy asphalt at low temperature. In the hot summer weather, the temperature is more than 60°C for bridge deck. The experimental results indicated that the similar softening point is achieved between curing 24 h at 60°C and curing

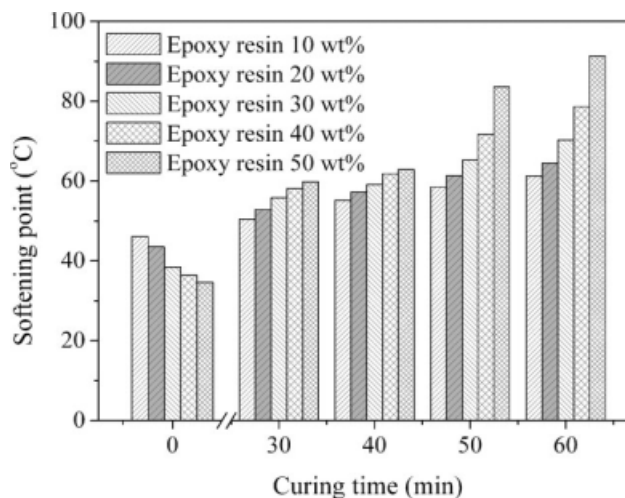


Figure 3 Effect of curing temperature on softening point at 120°C.

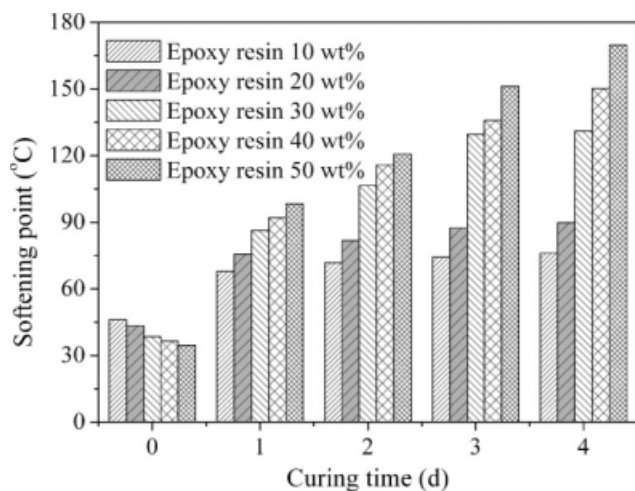


Figure 4 Effect of curing temperature on softening point at 60°C.

60 min at 120°C. Thus, epoxy asphalt can cure at low temperature (60°C) and operation temperature and time must control strictly to obtain optimal properties.

Most modified asphalt binders are non-Newtonian fluids at mixing and compacting temperature range *in situ* currently. The effect of viscosity on asphalt binder's workability is very important in selecting proper mixing and compacting temperatures. Epoxy asphalt is a thermosetting material. The mixing time is carefully controlled so that it is long enough to give a uniform coating of epoxy asphalt to all aggregates and short enough to prevent epoxy asphalt hardening due to chemical reaction during building. Figure 5 shows the effect of curing time on viscosity of epoxy asphalt with different epoxy resin content at 120°C. It is well known that the curing reaction will result in increasing of epoxy asphalt's viscosity and the more the epoxy resin content in asphalt, the

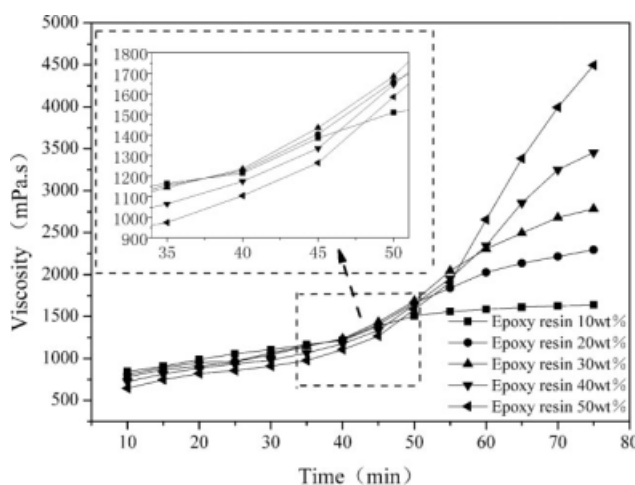


Figure 5 Effect of curing time on viscosity of epoxy asphalt.

greater the viscosity. However, there was no notable difference for epoxy asphalt with different epoxy resin content when curing time was not more than 50 min. This is because that the viscosity of uncured epoxy resin was lower than that of original asphalt at 120°C, thus the viscosity of the blending of asphalt and epoxy resin was decreased before curing and the decrease of viscosity was directly proportional to the epoxy resin concentration.

According to Figure 5, the original viscosity of all epoxy asphalt was about 600–800 mPa s and the viscosity was less than 2 Pa s at 50 min curing time at 120°C. For SBS modified asphalt mixture, appropriate asphalt's viscosity is 600–800 mPa s for blending the mixture and suitable asphalt's viscosity is about 2 Pa s to compact the mixture. Kevin and Donn²⁵ believed that the optimum viscosity range for epoxy asphalt is also 2–3 Pa s for compacting epoxy asphalt mixture. If viscosity of epoxy asphalt exceeds 3 Pa s, the mixture becomes too hard to compact the pavement and it is difficult to form an eligible pavement surface. Therefore, epoxy asphalt mixture must control strictly operation time and the compacting must complete before the viscosity reaches 3 Pa s.

Figure 6 gives FTIR spectra of modified asphalt with 40 wt % epoxy resin during curing at 120°C. The evolution of the selected bands with curing time for the 2000–500 cm^{-1} interval can be observed in Figure 6. The principal FTIR absorption bands of epoxy asphalt are listed in Table II. Epoxy asphalt that cured at the beginning also showed a tiny peak around 1700 cm^{-1} , which should be attributed to carbonyl or carboxylic of asphalt.^{27–30} The most important of these peaks is that of the epoxy band at

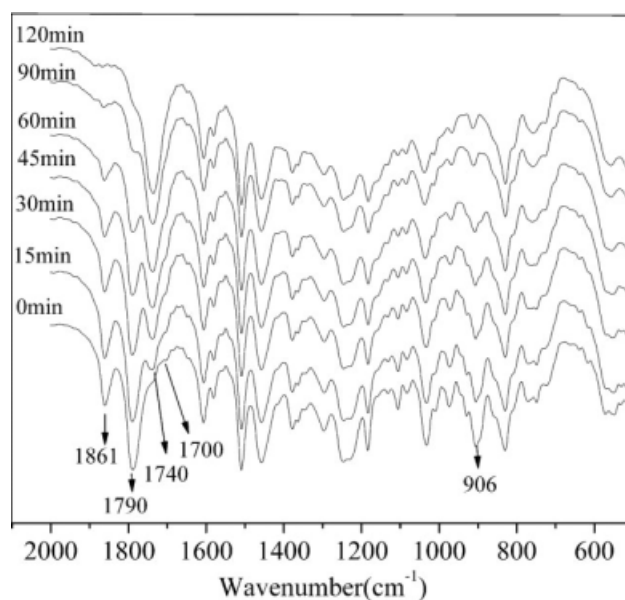


Figure 6 FTIR spectra of epoxy asphalt for different curing time at 120°C.

TABLE II
Epoxy Asphalt IR Absorption Bands

Functional group	Wavenumber/cm ⁻¹
<i>p</i> -phenylene groups	830
Epoxy band	1509
Acid anhydride bands	906
	1861
	1790
Carbonyl/carboxylic	1700
Ester carbonyl	1740
Aliphatic carbon–oxygen stretching	1035

906 cm⁻¹. Thus, the change of epoxy group peak was followed at 120°C. After cure reaction began, the peak value of characteristic acid anhydride bands at 1861 cm⁻¹ and 1790 cm⁻¹ and the epoxy resin characteristic band at 906 cm⁻¹ decreased with curing time, and a new band at 1740 cm⁻¹ appeared, which was attributed to ester carbonyl of cured product. At the same time, the tiny peak around 1700 cm⁻¹ disappeared during curing reaction, which means that curing reaction can also take place between epoxy resin and asphalt.³¹ The results indicated that the operation time and temperature must control strictly when epoxy asphalt was selected to prepared epoxy asphalt mixture.

Mechanical property

Tensile strength and elongation at break for epoxy asphalts is shown in Figure 7. The tensile strength of epoxy asphalt increased with epoxy resin content increase. The tensile strength of epoxy asphalt increased slowly when epoxy resin content was lower than 20 wt %; however, it is still higher than that of original SBS modified asphalt. The tensile strength markedly increased when epoxy asphalt content exceeded 20 wt %. For example, the tensile strength of epoxy asphalt with 10, 20, and 30 wt % epoxy resin was 0.32, 0.41, and 1.24 MPa, respectively.

The parameter, elongation at break, is one of the key elements in predicting epoxy asphalt's ductility. The elongation at break of epoxy asphalt with different epoxy resin concentration is showed in Figure 7. The elongation at break of epoxy asphalt with 10 wt % epoxy resin was 440%, but it was only 130% when 50 wt % epoxy resin was mixed with asphalt. The results shown that the elongation at break of epoxy asphalt decreased significantly as the epoxy resin concentration increased. Original asphalt is SBS modified asphalt and it is rubber-like elastic materials. Thus, the elongation at break of original asphalt is very large when compared with epoxy asphalt. But the cured epoxy resin destroyed the deformability of original asphalt.

Morphology

The morphology of epoxy asphalt was studied by fluorescent microscope to characterize the nature of the continuous phase and discontinuous phase. As shown in Figure 8 blends of epoxy resin and asphalt exhibit a multiphase morphology. The light phase in the picture represents the SBS and epoxy resin, and the dark phase is the asphalt. SBS is dispersed as small particles in the asphalt as shown in Figure 8(a). The images show a clear change in morphology of the epoxy asphalt as the epoxy resin content increases. When the content of epoxy resin is lower, the SBS and epoxy resin that segregates into small regions and these small regions are called the discrete phase as shown in Figure 8(a–c). For 30% epoxy resin content, the epoxy resin and asphalt are continuous and interlocked as illustrated in Figure 8(d). At this moment the epoxy resin phase gradually become the matrix of the system, and the epoxy asphalt starts the phase inversion. This phase inversion results from the epoxy resin content increase in epoxy asphalt. The epoxy resin is a thermoset material. When the epoxy resin phase forms the continuous as shown in Figure 8(d), the properties of the mixture are mainly determined by the epoxy resin. Such systems generally pose higher cohesive and strength. Figure 6 confirms the tensile strength of epoxy asphalt increase than that low content epoxy asphalt. At higher epoxy resin content, a continuous epoxy resin phase with dispersed asphalt phase is observed. Figure 8(e,f) demonstrates that the epoxy resin is the continuous phase of the system, and the asphalt is homogeneously dispersed phase. The combination of these three constituent materials yields epoxy asphalt in which SBS, epoxy resin, and asphalt are combined to result in a material that has properties different from those of either constituent.

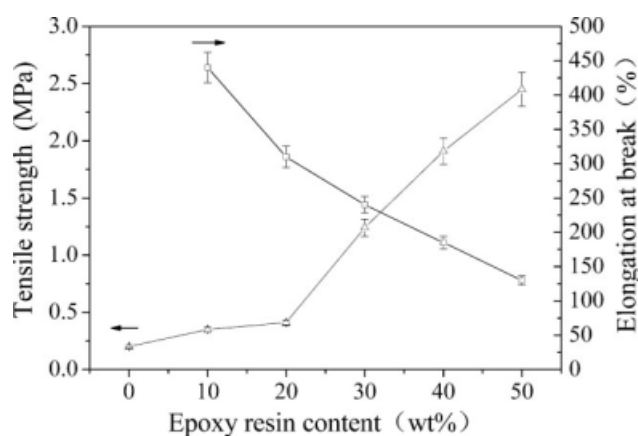


Figure 7 Effect of epoxy resin content on mechanical property.

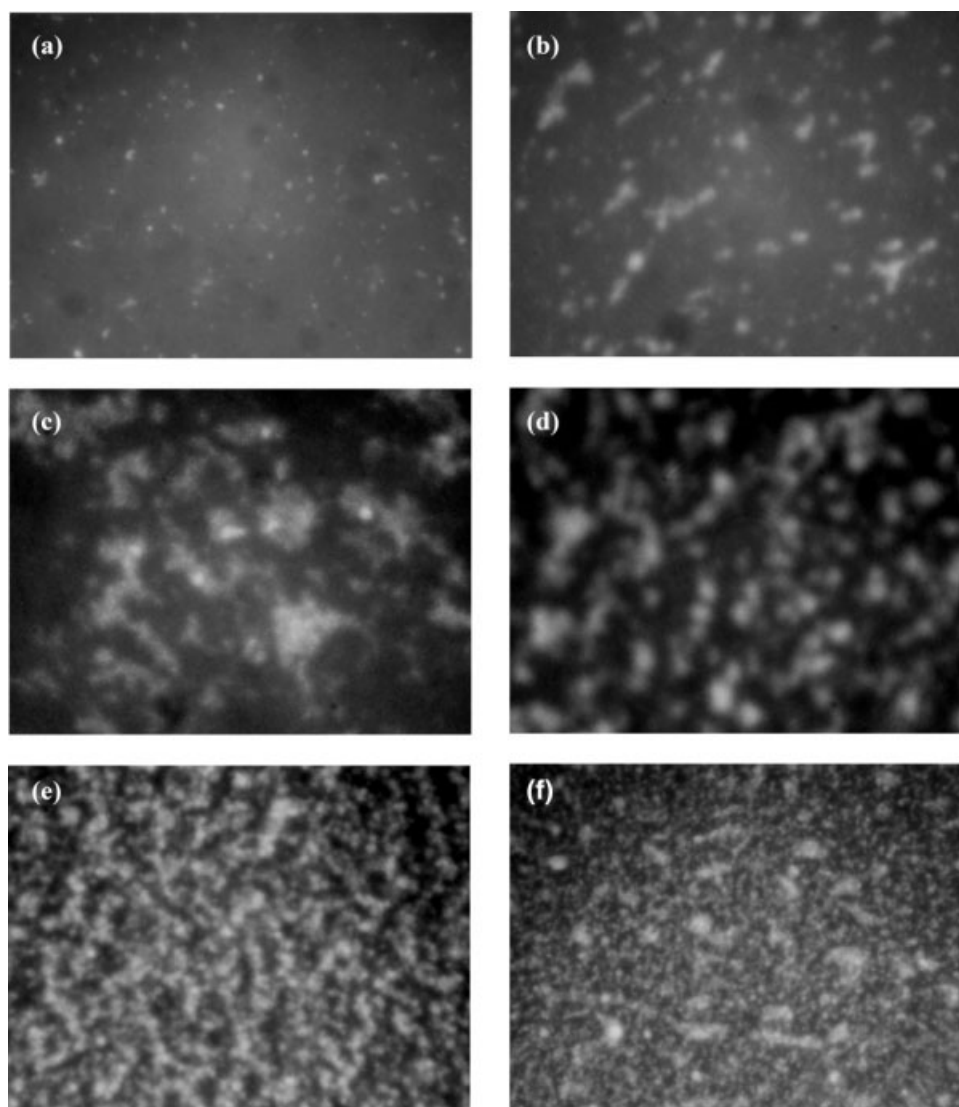


Figure 8 Fluorescent micrograph of epoxy asphalt containing epoxy resin content of (a) 0 wt %, (b) 10 wt %, (c) 20 wt %, (d) 30 wt % (e) 40 wt %, and (f) 50 wt %.

CONCLUSIONS

Epoxy asphalts were prepared by blending SBS modified asphalt with diglycidyl ether of Bisphenol A and MTHPA curing agent. Asphalt in epoxy asphalt has a little effect on the optimum ratio of curing agent to epoxy resin. FTIR analysis indicated that epoxy resin reacts with not only curing agent but also carboxylic acid in epoxy asphalt. Fluorescent microscope indicated that epoxy resin was dispersed in asphalt when the epoxy resin content was less than 30 wt %. The epoxy asphalt began forming networks structure when 30 wt % epoxy resin blend with asphalt. In addition, the epoxy resin phase gradually became the principle phase with epoxy resin contents continuously increasing.

The epoxy asphalt can be cured not only at 120°C but also at 60°C. The initializing viscosity of epoxy asphalts was about 600–800 mPa s, it was not more

than 2 Pa s for 60 min at 120°C. The change of viscosity can meet the demands of epoxy asphalt mixture blending and compacting.

The mechanical properties revealed that the tensile strength increased significantly when the contents of epoxy resin were more than 30 wt %, which is attributed to the formation of continuous networks structure in epoxy asphalt. But the elongation at break of epoxy asphalt decreased as the epoxy resin concentration increased.

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