Effects of Epoxy Resin Contents on the Rheological Properties of Epoxy-Asphalt Blends

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ABSTRACT: Epoxy-asphalt and its mixture have been proposed for the long span orthotropic steel deck bridges because it shows excellent heat resistance, free from bleeding, low temperature cracking resistance, and aggregate scattering resistance. In this study, the effects of epoxy resin contents on rheological properties of epoxy-asphalt binders were studied using dynamic shear rheometer. Experimental results indicated that the improvement of the viscoelastic performance of asphalt binder is noticeable at high temperatures, at which the elasticity is increased (higher G^* and lower δ) for epoxy-asphalt with increase in epoxy resin contents. The viscous behavior of the asphalt also increased when epoxy resin is added. Creep test results indicated that epoxy-asphalt binder can not only resist deformation at elevated temperatures but recover satisfactorily from strain. J Appl Polym Sci 118: 3678–3684, 2010

Key words: asphalt; epoxy resin; rheology; viscoelastic; creep; permanent deformation

INTRODUCTION

Epoxy-asphalts have better mechanical properties and high temperature stability than the nonmodified ones.[1–3] In 1967, epoxy-asphalt mixture was used on San Mateo-Hayward Bridge in the San Francisco Bay and nowadays it is increasingly used in the steel deck pavement.[4] Epoxy resin can improve asphalt mixtures resistance to rutting, fatigue and flow at medium, and high temperatures. But epoxy resin in the modified asphalt binder should neither make asphalt binder too viscous at processing temperature nor too brittle at low temperatures.[5,6] Furthermore, epoxy-asphalt must have good stability during transportation in order to guarantee better mechanical properties than pure asphalt.

Epoxy-asphalt is a thermosetting material and the classical tests methods applied for pure asphalt specifications are not sufficient to well characterize the blend.[7–9] Many investigators have suggested the use of rheological tests to predict the performance of modified asphalt. This test gives more reliable information about the asphalt binders. The dynamic shear rheometer is employed to characterize the rheological properties of asphalt binders. The shearing frequencies used in the sample characterization can be correlated to traffic conditions.[10–13] Frequencies between 10^{-1} and 10^2 rad/s are used to simulate the normal vehicle traffic on the pavement. Two important parameters obtained from rheological tests in dynamic mode are the complex modulus (G^*) and the phase angle (δ). The former can be related to the material strength and the latter provides information about the ratio between elastic and viscous response during the shearing process. Creep compliance is a fundamental material property that represents the rheological behavior of viscoelastic materials.[14–17] Accurate determination of the creep compliance of asphalt is crucial to evaluate the time/frequence dependent stress and strain response.[18–20] Under small strain levels, the rheological behavior of neat asphalt shows linear behavior so that it can be generalized as a linear viscoelastic material. At low temperatures (or short loading times), the behavior of asphalt approaches the behavior of elastic solids. But a weak viscoelastic behavior is observed when the temperature is increased. Epoxy resin shifts asphalt's properties to more solid-like. The contents of epoxy resin have a much greater impact on the reheological properties of asphalt.

In this work, a set of epoxy-asphalt was prepared in the laboratory. The original asphalt binders and epoxy-asphalt were analyzed by dynamic shear rheometer. The aim of this work was to study the effect of the contents of epoxy resin on the linear

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viscoelastic properties of asphalt and to correlate these properties to the epoxy-asphalt thermal susceptibility.

EXPERIMENTALS

Raw materials

The 60/80 pen grade asphalt used was obtained from Guochuang Asphalt in Huber province, China, with penetration of 77 (0.1 mm at 25°C 100 g and 5s), softening point of 45.9°C, ductility of 118 cm (at 15°C), and viscosity of 0.5 Pa s (at 135°C). SBS used grade 1301 was produced by the Yueyang Petrochemical, China. This was a linear-like SBS, containing 30 wt % styrene, and the weight-average molecular weight of Styrene-Butadiene-Styrene triblock copolymer (SBS) is 1,20,000. The epoxy resin used was diglycidyl ether of bisphenol A and its epoxy value is 0.52 mol/100 g. It was obtained from Shanghai Xinhua Resin, Shanghai, China. Methyl tetrahydro phthalic anhydride curing agent was provided by Jiaxing Fine Chemical, Zhejiang province, China. All materials were commercially available and used as received.

Methods

Asphalt was heated to 170 ± 5°C in an oil bath heating container until it flowed fully. Then 3% by weight of SBS was mixed into the asphalt under high rotation speed (usually 8000 rpm) for 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 (preheated to 120°C) was added into the blend and stirring continued for 5 min under the same mixing condition. Then the sample for test was prepared in accordance with standardized procedure, and cooled in a refrigerator for about 30 min at 0°C. Epoxy-asphalts with 10, 20, 30, 40, and 50 wt % epoxy resin (including curing agent) were prepared, respectively.

Dynamic shear properties were measured with Physical MCR 101 dynamic shear rheometer (Anton Paar, Austria) in a parallel plate with 1 mm gap and 25 mm diameter. A DSR temperature sweep test was performed under the strain controlled mode at a constant frequency of 10 rad/s. All tests were performed within the linear viscoelastic range. Test temperature varied from 30 to 100°C with 2°C increment per minute. Frequency sweeps at 0.1 to 100 rad/s were also performed for each sample at 60°C. Complex modulus and phase angle at different temperatures were recorded automatically during the test.

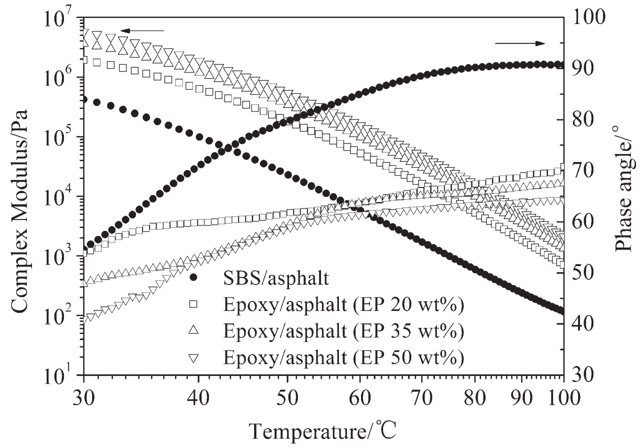

Figure 1 Relation of temperature and complex modulus and phase angle at 10 rad/sec asphalt and epoxy-asphalt.

Shear creep properties of asphalt binder were tested using the same MCR 101 dynamic shear rheometer with similar samples as described above. The sample was subjected to a sequence of shear loading and unloading. The strain response, as a function of time, was measured and expressed by accumulated strain. Consistent with the test protocol, two creep loads were chosen at 400 and 1000 Pa. The loading time was 100 s with a recovery (unloading) time of 400 s, respectively. The test temperatures were 40 and 60°C.

RESULTS AND DISCUSSION

G^* and δ versus temperature

Figure 1 shows the temperature dependency of complex modulus (G^*) and phase angle (δ) at 10 rad/sec for each binder in a range of temperature 30–100°C. The obtained results indicate that epoxy-asphalt binders show an increase in the complex modulus compared to the original binder and the higher the epoxy resin contents, the higher the increase, especially at relatively high temperatures. As a result, the slope of the G^*-temperature curve decreases with increase in the epoxy resin contents, meaning that epoxy resin makes the asphalt binder less temperature sensitive in G^*. Phase angle is another very important rheological parameter for asphalt binders. The desired effect of epoxy resin is to provide an epoxy resin continuous phase that imparts elastic stability at higher temperatures and this is indicated by a decrease in phase angle. Figure 1 also shows phase angle curves for original and epoxy-asphalt binders. It is clear that the addition of epoxy resin to asphalt

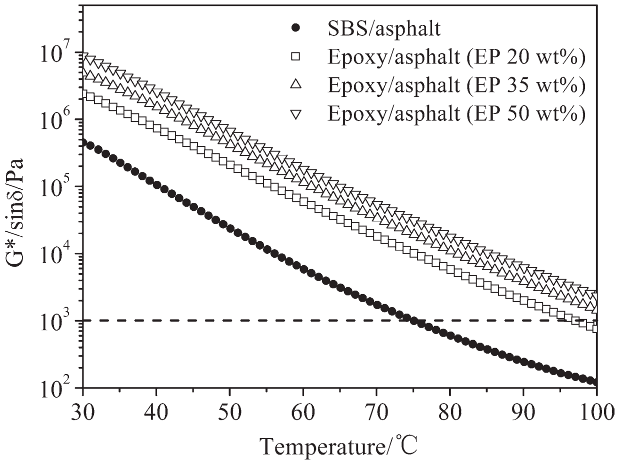

Figure 2 Relation of temperature and $G^*/\sin\delta$ at 10 rad/sec asphalt and epoxy-asphalt.

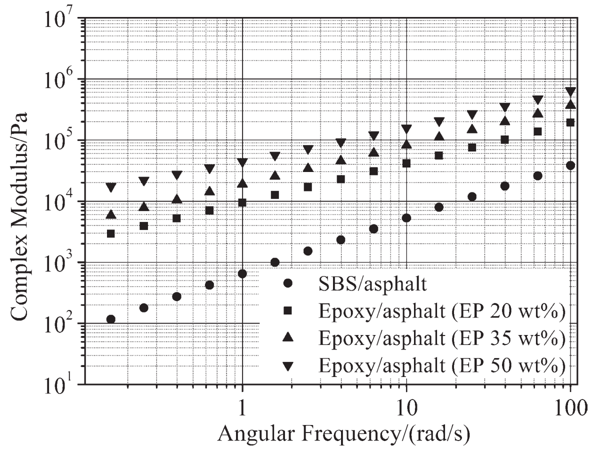

Figure 3 Effects of frequency on the G^* of asphalt and epoxy-asphalt at 60°C.

decreases the phase angle value significantly, meaning that epoxy resin imparts elasticity to the original asphalt. The phase angle of epoxy-asphalt increases slightly with temperature implying that epoxy resin decreases the temperature sensitivity of asphalt binder. Thus, the improvement of the viscoelastic performance is noticeable at high temperatures, at which the elasticity is increased (higher G^* and lower δ) for the asphalt modified with the epoxy resin.

Rutting parameter

The Strategic Highway Research Program (SHRP) tests used the rheological measurements as a tool to analyze the properties of asphalt binders used in road pavements. Plots of rutting parameter ($G^*/\sin\delta$) versus temperature are displayed in Figure 2. According to the SHRP test, the temperature at which $G^*/\sin\delta = 1$ kPa marks the maximum temperature for a good viscoelastic performance of the asphalt binder in the pavement. The road pavements can undergo very high temperatures in southern China, which provoke permanent deformations or rutting defects. Results of Figure 2 reveal that the maximum temperature of rutting is enhanced when epoxy resin is used as a modifier. The maximum temperature of original asphalt is $\sim$ 75°C whereas for epoxy-asphalt binder containing 20 wt % epoxy resins the value is 96°C. This indicates that the epoxy-asphalt binders' performances are better than the original asphalt binder. It is also known that higher $G^*/\sin\delta$ values will result in higher rutting resistance. As shown in Figure 1, the epoxy resin increases the complex modulus and reduces the phase angle, thus changes the elasticity of the modified binder. It is observed that the increase in $G^*/\sin\delta$ by epoxy resin was mainly caused by increase of G^* between these two factors above. The contribution of the phase angle (δ) to the rutting resistance is much less as compared to G^* due to a factor of $\sin\delta$. The reason for this is that, at such a test temperature region, $\sin\delta$ was observed to be in a relatively narrow range between 0.5 and 1 with a phase angle of 30–90, while G* values vary over a much wider range.

G^* and δ versus angular frequency

The effect of the epoxy resin on G^* and δ of asphalt binders at 60°C can be observed in Figures 3 and 4. Consistent with Figure 1 results, the epoxy-asphalt presented higher complex modulus than original asphalt binders in the whole range of frequencies studied. And compared to original asphalt binder, epoxy-asphalt showed a marked increase in the complex modulus at low angular frequency (high temperature). As a result, the slop of G^* decreased with increasing epoxy resin content. This increase in asphalt binder's modulus due to epoxy resin addition occurs because epoxy resin has higher modulus than the original asphalt binders.

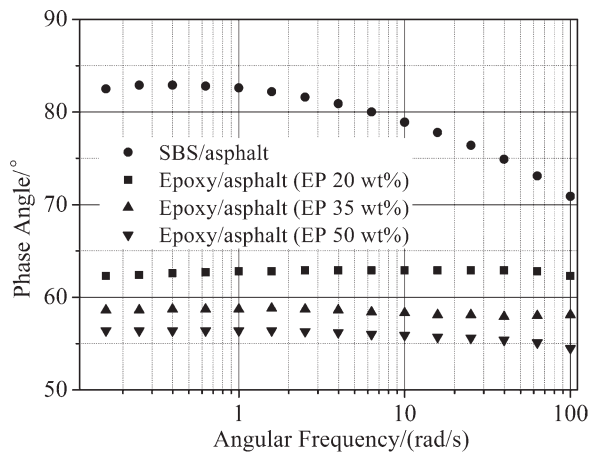

Figure 4 Effects of frequency on the phase angle of asphalt and epoxy-asphalt at 60°C.

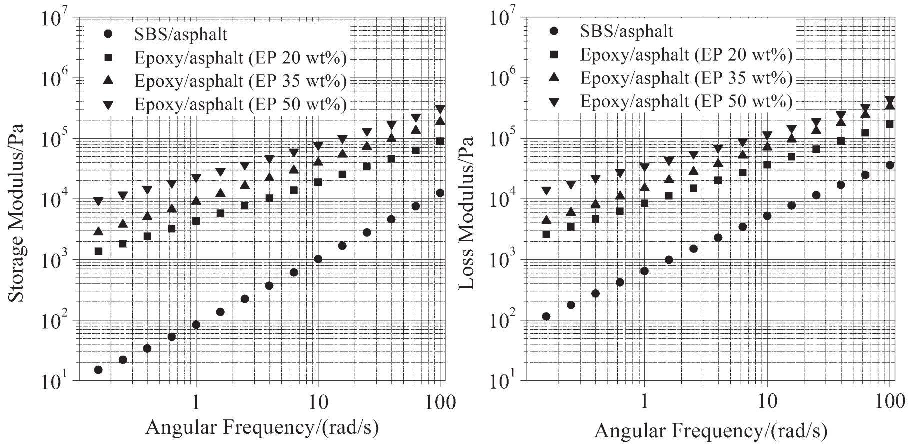

Figure 5 Effects of frequency on the storage modulus and loss modulus of asphalt and epoxy-asphalt at 60°C.

Figure 4 show δ versus angular frequency for original and epoxy-asphalt binder. It can be observed that there was a drastic change in the shape of the phase angle curves when epoxy resin is added in the asphalt binder. The epoxy resin has caused an approximately leveled off phase angle curves. This means that the elastic (G') and viscous (G'') complex modulus components vary in the same proportion in such a way that the phase angle does not change ($\tan\delta = G''/G'$). Then, the results indicate that the epoxy resin decreases the asphalt's angular frequency and the elastic component is constant in a broader range of angular frenquecy than that of the original asphalt binder. It also means that epoxy resin gives more effective contribution of the elastomeric modifier to the asphalt binder mechanical response.

G' and G'' versus angular frequency

Epoxy-asphalt is expected to have better low temperature cracking resistance. Storage modulus and loss modulus for original and epoxy-asphalt binders are shown in Figure 5, where all data have been obtained at 60°C. It can be seen in Figure 5 that the epoxy-asphalt at 60°C is more elastic than the original asphalt. The storage modulus increases more than loss modulus when epoxy resin is added into asphalt. In other words, the elastic and viscous behavior of the asphalt both increase, but the increase in the elastic component was higher. Thus, epoxy-asphalt has better deformation resistance at high temperature and better cracking resistance at low temperature.

Creep and recovery

The high quality asphalt binder can not only just resist permanent deformation at elevated temperatures but also recover satisfactorily from various forms of stresses imposed onto it to remain sufficiently elastic at a broad range of temperatures. The

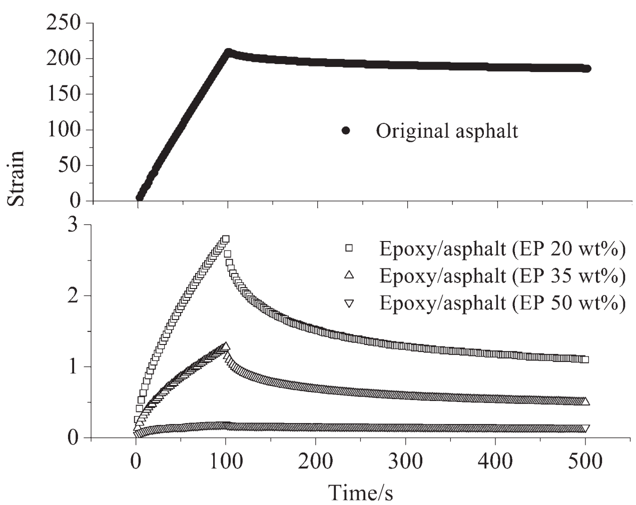

Figure 6 Creep strain curves for asphalt and epoxy-asphalt at 40°C and 400 Pa.

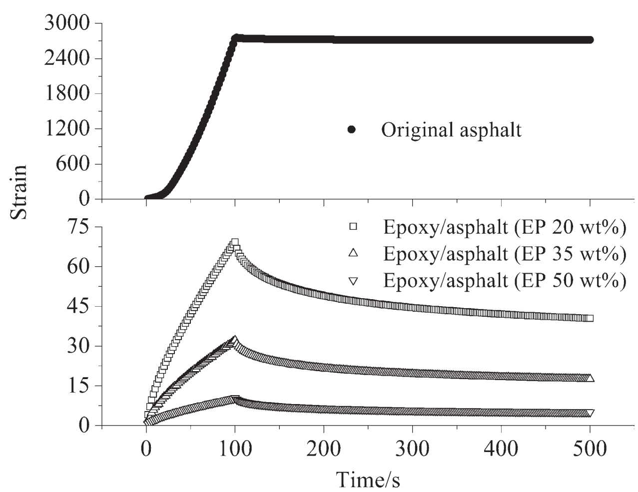

Figure 7 Creep strain curves for asphalt and epoxy-asphalt at 60°C and 400 Pa.

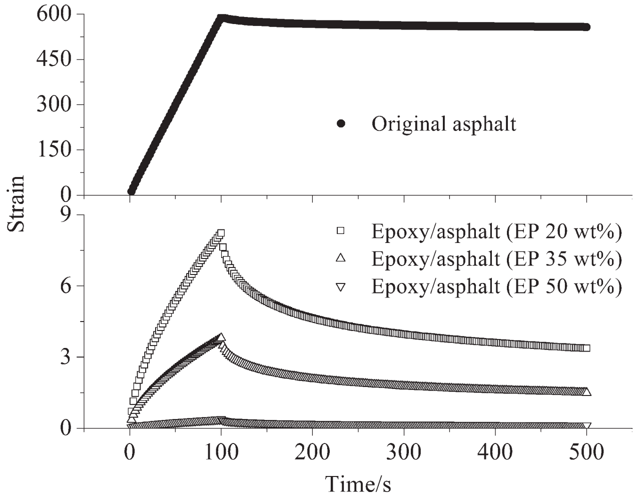

Figure 8 Creep strain curves for asphalt and epoxy-asphalt at 40°C and 1000 Pa.

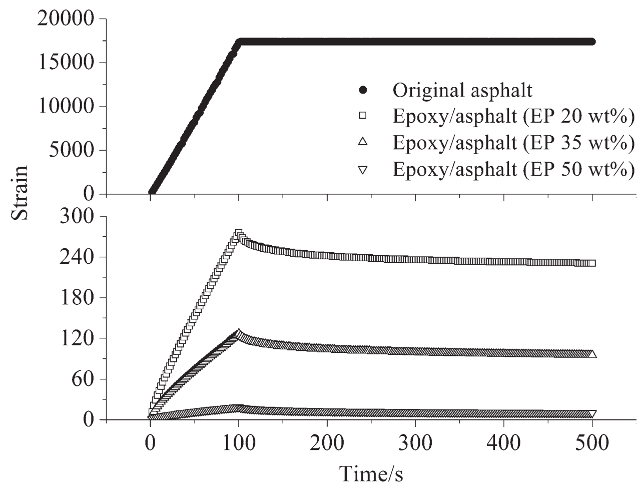

Figure 9 Creep strain curves for asphalt and epoxy-asphalt at 60°C and 1000 Pa.

ability of the original and three epoxy-asphalt binders to recover with the different stresses at different temperatures are depicted in Figures 6–9. The loading time is 100 s and the rebound time is 400 s. When the load is applied, a strain attributing to the elastic deformation appears instantaneously. In the load duration ($0 < t < 100$ s), the strains containing viscoelastic and viscoplastic components occur. Once the load is removed ($t = 100$ s), the elastic strain is recovered instantaneously. In the rebound period ($100 < t < 500$ s), the recoverable strain is recovered.

The creep results indicated that the strain of the original asphalt is larger than epoxy-asphalt at the same stress and temperature. It is indicated that epoxy resin can decrease the total strain of asphalt and increase elastic deformation and recoverable deformation. So the permanent deformation of asphalt binder was decreased when epoxy resin was added into asphalt, and the decrease of permanent deformation is higher at higher epoxy resin contents. The creep strain showed similar change when the different stresses were applied. But the original asphalt and epoxy-asphalt showed better recovery from strain when the temperature is low and the stress is small enough.

The total strain at load duration, permanent strain, and recovery ratio of strain are shown in Table I for original asphalt and the epoxy-asphalt blends at different temperatures and stresses. The results indicated that the effect of epoxy resin on creep properties is significant. At 40°C the recovery ratio of strain of the asphalt binders is increased when epoxy resin is added whereas the ratio enhances insignificantly with epoxy content. The original asphalt binder exhibits hardly any recovery when the temperature is higher than 40°C or the stress is higher than 400 Pa. The epoxy-asphalt showed higher recovery ratios at these conditions also. The parameter was quite similar up to 35% epoxy content, however the value is higher at 50% epoxy content. Thus, epoxy-asphalt binders can not only resist permanent

TABLE I
Strain and Recovery Ratio of Deformation for Original and Epoxy-Asphalt Binder

Experimental condition				Epoxy-Asphalt containing		
Temperature	Load	Deformation	Original asphalt	EP 20 wt %	EP 35 wt %	EP 50 wt %
40°C	400 Pa	Total strain	209	2.8	1.28	0.19
		Permanent strain	186	1.1	0.5	0.07
		Recovery ratio	11.0%	60.7%	60.9%	63.2%
60°C	400 Pa	Total strain	2730	49	21.6	6.54
		Permanent strain	2720	40.5	17.6	5.1
		Recovery ratio	0.37%	17.4%	18.5%	22.0%
40°C	1000 Pa	Total strain	568	4.64	2.08	0.2
		Permanent strain	557	3.38	1.5	0.1
		Recovery ratio	1.9%	27.2%	27.9%	50.0%
60°C	1000 Pa	Total strain	17400	242	104	12.8
		Permanent strain	17400	231	95.7	10.3
		Recovery ratio	0	4.6%	8.0%	19.5%

deformation at elevated temperatures but also recover satisfactorily from strain.

Creep compliance

Creep compliance is the ratio of the strain to the applied stress, which reflects the softness (or pliability) of the material. Figure 10 show plots of creep compliance as a function of time, for original asphalt binder and epoxy-asphalt containing different quantities of epoxy resin at stresses 400 Pa and 1000 Pa at 40°C. It can be noted that the creep compliance of the original asphalt was much higher than that of the epoxy-asphalt. The reasons for such behavior were the main deformation of original asphalt binder is viscous deformation at 40°C, Figures 6 and 8. Figure 10 shows that the creep compliance of asphalt binder is equal for the same asphalt binder with different stress. The same tests were performed, as Figure 11 showed. Asphalt binder is unaffected with the variation of stress. The creep compliance-time plots at 60°C and stresses 400 and 1000 Pa showed similar variations, the data were higher, however. Independence between stress and compliance is the prerequisite to confirm materials possessing linear viscoelastic behavior. The creep compliance results indicated that the compliance does not change with stress. Thus, the original asphalt and epoxy-asphalt binders can be considered as linear viscoelastic materials at test conditions. But the compliance of the original asphalt and epoxy-asphalt do not show absolutely linear increase with time. They all showed delayed elastic behavior. As Figures 10 and 11 showed, the effect of temperature on creep compliance is very high for the original asphalt binder. The epoxy resin can decrease this effect and the higher the epoxy resin content the higher the decrease. Thus, the creep compliance results indicated that the epoxy resin can decrease temperature sensitively of asphalt.

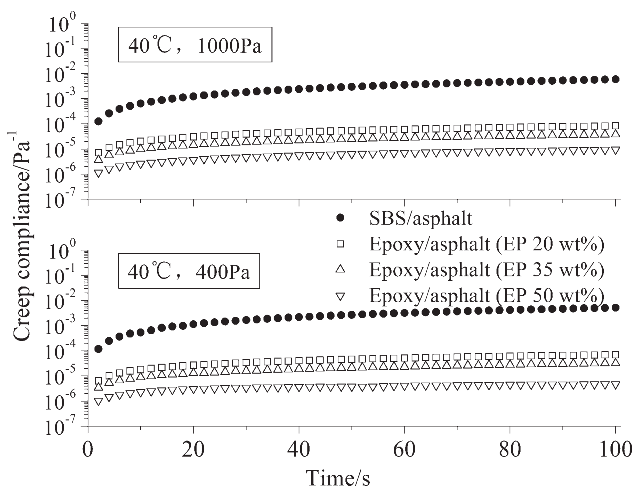

Figure 10 Creep compliance of asphalt and epoxy-asphalt at 40°C.

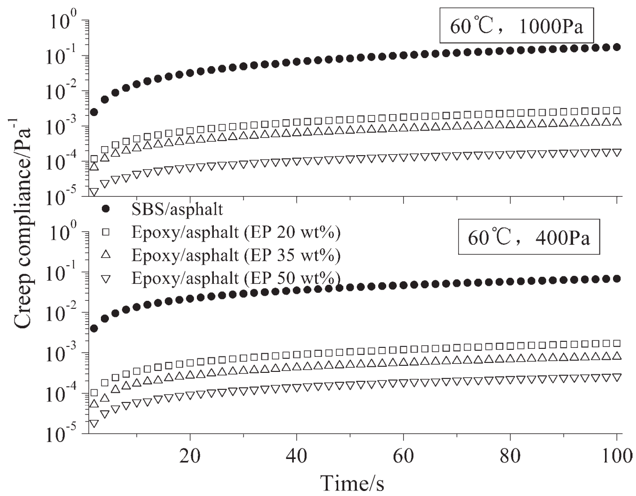

Figure 11 Creep compliance of asphalt and epoxy-asphalt at 60°C.

CONCLUSIONS

Asphalt is a thermoplastic material. Because of its thermoplastic nature, asphalts are limited to applications where the asphalt can not tolerate excessive heat. By blending the epoxy resin with asphalt, a new material with better heat resistance and high strength is obtained. In this study, the effects of epoxy resin contents on rheological properties of epoxy-asphalt binders were tested using dynamic shear rheometer. Compared to original asphalt binder, the complex modulus of epoxy-asphalt containing 20 wt % epoxy resin is order of magnitude higher than the original ones. Epoxy resin also affects phase angle significantly, and the higher the epoxy resin contents the higher the effect. Besides the increased permanent deformation resistance at high temperature, epoxy resin also improves the recovery from strain and decreases temperature sensitivity of asphalt.

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