

Preparation and characterization of epoxy asphalt binder for pavement of steel deck bridge

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Abstract: A kind of thermosetting asphalt binder designated as epoxy asphalt, which is composed of two components: maleated asphalt with curing agents and accelerant of epoxy resin and epoxy resin, was prepared. Its paving feasibility and concrete performances were investigated using Brookfield viscosimeter, direct tensile test (DTT), Marshall testing and the MTS 810 hydraulic servos-system, respectively. Although only 50% to 60% of added maleic anhydride (MAH) reacted with the base asphalt irreversibly (probably by Diels-Alder mechanism), the curing rate, rupture elongation and tensile strength of maleated epoxy asphalt were enhanced more evidently than those of unmaleated epoxy asphalt. As a result, an epoxy asphalt made from 4% MAH modified asphalt and other curing agents was featured to have an average rupture elongation of 281.9%, an average tensile strength of 2.63 MPa, and the Marshall stability of its cured concrete reached 37.0 kN, while that of uncured concrete was 10.2 kN and the combined beam of fatigue test was still found to behave well after 12×10^6 cycles load.

Key words: epoxy asphalt; preparation; characterization

Asphalt has both viscous properties, which allow flow, and elastic properties, which resist flow. At high temperature, the viscous properties dominate and the asphalt tends to flow or deform, while at low temperature, the elastic properties dominate and the asphalt tends to resist flow. Compared with the base asphalt material, polymer-modified asphalts (PMAs) have reduced thermal susceptibility and permanent deformation, and have enhanced resistance to low-temperature cracking. As a result, PMAs have been widely used in road paving. Generally, methods used for asphalt modification can be grouped into two main categories: physical co-blends and chemical modifications. Belonging to the first category, the styrene-butadiene-styrene block (SBS) copolymer^[1-3] is probably the most frequently used asphalt modifier for paving applications, and polyethylene (PE), ethylene-vinyl acetate (EVA), ethylene-butyl acrylate (EBA) random copolymers etc.^[4-7] are the other examples. To improve the storage stability, reactive polymers have been introduced as asphalt modifiers. Examples of reactive polymers are thermoplastic elastomers functionalized with maleic anhydride^[8] and ethylene-based copolymers containing epoxy rings^[9-10].

Due to its high strength and stiffness, the orthotropic steel deck system has been widely used in the con-

struction of long-span steel bridges. Consequently, its pavement has become very important in recent years and has not been well solved since the stress and deformation of the steel decks' surfaces are much more complex than those of the highways and airport surfaces. Asphalt composites for use in steel deck bridges must possess certain characteristics. For example, they should provide a high resistance to varying climatic conditions, heat, wear and a variety of solvents that come into contact with such surfaces. Moreover, they must meet all the foregoing requirements without adversely affecting the skid properties, traction strength and final hardness of the surfaces.

Although the adoption of the above-mentioned modifiers results in somewhat improvement of the properties of the asphalt concrete, they cannot satisfy the rigorous demands of the steel deck bridge surface paving because of their thermoplastic natures. In the year of 1996, essentially different from the so-called general modified asphalt, a novel concept of thermosetting asphalt^[11-12] was proposed as heat-curable coating or molding compositions. This kind of thermosetting asphalt possesses true thermosetting characteristics. It does not flow or melt upon an increase in temperature, and, in fact, it has no softening point below the decomposition temperature. In addition, the thermosetting asphalt provides improvements in solvent resistance and toughness compared with the conventional asphalt.

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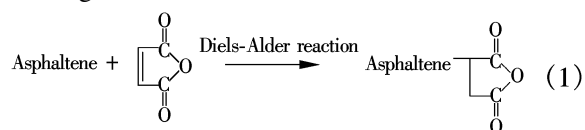
Even though epoxy resin is the most common sort of thermosetting resins, it is incompatible with road construction asphalt. Early in 1961, Mika^[13] presented the two-component epoxy-asphalt composites containing pine tar as compatilizer and found that these composites when cured form homogenous insoluble, infusible products. From then on, one-component^[14–15] or three-component^[16] epoxy-asphalt composites were developed one after another, and compatilizer^[17] was also invented. However, the one-component epoxy-asphalt composites have bad storage stability, and the three-component products are difficult to popularize due to its complex production process.

In 1979, Hayashi et al.^[18] prepared an asphalt composite comprising a) an epoxy resin and b) a maleated asphaltic material by reacting asphalt directly with maleic anhydride and a curing agent polyamine for the epoxy resin. However the maleated asphalt easily reacting with the curing agent polyamine resulted in poor stability of component b). At the same time, Doi et al.^[19] reported another composite comprising a) a heated asphalt and b) epoxy resin and an amine having two active hydrogens. Nevertheless, the epoxy resin readily reacting with the amine still resulted in poor stability of the component b). Furthermore, epoxy resin and the asphalt tend to separate from each other due to their poor compatibility, and the curing of the mixture is ineffective since only the resin is cured without forming the cured composites of uniform quality. Over ten years later, Gallagher et al.^[11–12], who advocated “thermosetting asphalt” clearly for the first time, presented another two-components thermosetting asphalt a) asphalt and epoxy-functionalized polymers and b) a second asphalt which is chemically modified by incorporating one or more of the group comprising amines, anhydride, alcohols, carboxylic acids and thiols.

There is no doubt that these inventions made great progress in thermosetting asphalt; however, they were focused on coating applications rather than paving applications. Thus, they did not take into consideration the time of workability for the paving purpose, which is critical in contrast to the thermoplastic asphalt. From the viewpoint of engineering, the time for preparation of the asphalt binder and the transportation of the asphalt concrete from the manufacturing plant to the paving spot is about 1 h. It is required that, during this period, the binder should have a relatively low viscosity. This time of workability is defined as the pot life.

To solve all the above problems completely, we propose that the base asphalt be modified with maleic

anhydride (MAH)^[20], firstly to obtain the maleated asphalt, which can be cured by the epoxy resin so as to improve the compatibility of asphalt and epoxy resin and also avoid asphalt bleeding from the curing product to the most degree. Afterwards, a kind of fatty acid and another kind of organic liquid anhydride are added as the curing agents in order to increase the flexibility and intensity. Furthermore, the maleated asphalt and the curing agents (organic acids and organic anhydride) can be preserved steadily. In addition, the curing time to serve the paving process can be controlled by means of adding some accelerant. In a word, this epoxy-asphalt composite composed of two components, epoxy resin and maleated asphalt with its curing agents, is a thermosetting composite when cured. This supposed mechanism is given below.



When used, the maleated asphalt as one of the curing agents was cured with the organic anhydride and organic carboxyl acid by the epoxy resin under the accelerant R_3N . The purpose of this study is to prepare and characterize this epoxy asphalt.

1 Experiment

1.1 Materials

Maleic anhydride (MAH), succinic anhydride (SAH), EJS-100 organic acid, TYG-200 organic anhydride, CJJ-300 accelerant (tertiary amine) and shell asphalt were used as received.

1.2 Reaction procedure

Reactions were carried out in a wide-mouthed glass flask fitted with a mechanical stirrer, condenser (warm water refluxing, 75 to 85 °C), thermocouple and gas inlet for vacuum (0.05 MPa). Asphalt were heated to the reaction temperature (120 to 150 °C) and MAH added at one time with constant stirring and reacted for a period of time (4 to 6 h). The other reactants were added gradually in half an hour, and subsequently, the mixture was agitated for about 0.5 h. This end product is designated as component A, and the epoxy resin as component B. The specimens of Eq. (1) were removed at intervals of up to 5 h after the completed addition of reactants and then stored in airtight containers at ambient temperature. Control experiments were carried out as above in the absence of MAH and with the substitution SAH for MAH.

1.3 Determination of MAH conversion

According to Ref. [20], the conversion of the MAH is about 50%. Also the MAH is perfectly soluble in a mixture of water and ethanol (volume ratio, 1 : 1), thus the free MAH can be extracted from a petroleum ether (90 to 120 °C) solution of the Eq. (1) specimens. The extract is titrated with aqueous KOH to a phenolphthalein end point^[21]. Then, the content of the free MAH of the Eq. (1) specimens can be calculated as

$$x = \frac{4.9NV}{m} \quad (2)$$

where x is the percentage by weight of the free MAH of the specimens; N and V are the equimolar concentration (N) and consumed volume (mL) of the titrant KOH, respectively; m is the sample weight (g).

1.4 Performance testing

Thermosetting asphalt is essentially different from the traditional thermoplastic asphalt, and thus their performance testing methods differ from each other. The dynamic shear rheometer (DSR), being the most important testing methods of the American Association of State Highway and Transportation Officials (AASHTO) are not suitable for this asphalt, as rheological measurement in the process of being cured of the binders is correspondingly important compared with the conventional asphalt binders due to its thermosetting properties. The first important task for the thermosetting asphalt as for paving purpose is to afford an appropriate time to manufacture the asphalt concrete and to pave it onto the road before it forms an insoluble, infusible asphalt gel.

1.4.1 Rheological measurement

Rheological measurement was carried out by means of Brookfield viscometer (DV-II, 29[#] rotor, 100 r/min) with an oil bath pan (120 °C) according to the procedures below. First, the apparatus and components A and B were heated to the testing temperature (120 °C), respectively. After A and B were quantified in a certain weight ratio and also kept warming, they were mixed and agitated for 1 min in a capped steel cup. And then, the viscosity values were recorded every 5 min.

1.4.2 Direct tensile test (DTT)

Components A and B were heated, mixed and sheared according to the procedures mentioned above, then, poured into the heated (120 °C) molds and baked (120 °C) in the oven to cure for 4 h. After they were cooled to the ambient temperature, the samples were taken out from the molds and kept heated at 20 °C for 1 h and cut into the standard shape. The direct tensile test

was carried out using an XLD-50A (grandtry) according to ASTM D638.

1.4.3 Examination of binder's thermosetting nature

The samples after DTT were placed onto hot plates at about 300 °C for 4 h.

1.4.4 Marshall testing

Components A and B were heated, mixed and agitated following the procedures mentioned above; afterwards, the binders were mixed with the specific gradation^[22] aggregates^[23] (asphalt aggregate ratio 6.5%). 40 min later, this epoxy asphalt concrete was placed in the Marshall mold. After having blown both sides of the samples 50 times, respectively, the uncured Marshall compaction sample was prepared. At the same time, another Marshall compaction sample was laid in the oven (120 °C) for 4 h to prepare the cured Marshall compaction sample. Then, Marshall testing was carried out according to JTJ052—2000.

1.4.5 Fatigue test

In order to characterize the fatigue resistance of the epoxy asphalt precisely, a combined beam that was made up of the steel deck with its pavement of epoxy asphalt as an integration was observed through MTS[®] 810 hydraulic servos-system. According to the computation of the finite element method, the load mode was sinusoidal waves 10 Hz, 5 kN^[23]. The specification of the testing combined beam specimens is as follows: total thickness 56 mm, width 10.8 mm, and the thickness of the steel deck 12.5 mm. After the combined beam was prepared and maintained at 120 °C for 4 h, the fatigue test was carried out.

2 Results and Discussion

2.1 Epoxy asphalt binder

2.1.1 Unmaleated epoxy asphalt binder

Fig. 1 clearly indicates that the increase of accelerant added in the unmaleated epoxy asphalt led to a

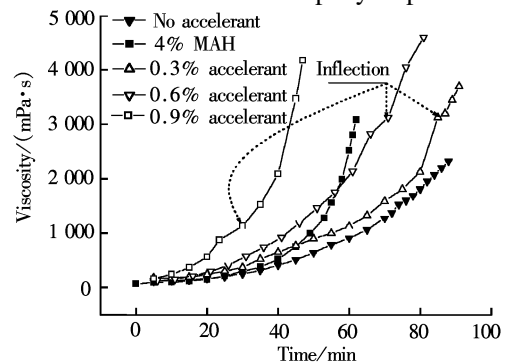


Fig. 1 Plots of viscosity vs. time in the curing of unmaleated epoxy asphalt with a range of accelerant concentration (120 °C)

great increase in its curing rate. However it was found that all the samples of unmaleated epoxy asphalt binders failed to cure in 4 h (see Tab. 1). This was unexpectedly. It implies that its traffic exposure is much slower than that of being cured in 4 h. It is suggested that the asphalt without maleation is filled instead of being linked with the network of the anhydride and acid cured product. Consequently, the chemical gel point does not appear in 4 h. It is also the reason that there are inflections on the curing curves of the unmaleated epoxy asphalt.

Tab. 1 Results of DTT under various conditions

Sample	Condition	Rupture elongation/%	Tensile strength/MPa
No. 1	4% MAH, 0.3% accelerant	281.9	2.63
No. 2	7% MAH, 0.3% accelerant	151.7	2.94
No. 3	4% SAH, 0.3% accelerant	Fail to cure in 4 h	
No. 4	No MAH or SAH, 0.6% accelerant	Fail to cure in 4 h	
No. 5	No MAH, 0.9% accelerant	Fail to cure in 4 h	
No. 6	4% MAH, no accelerant	Fail to cure in 4 h	

Based on the above results, it may be supposed that the initial higher viscosity of unmaleated epoxy asphalt binders causes the curing process to change from reaction control to diffusion control. Hence, the rheological measurement and DTT of (maleated) epoxy asphalt were carried out to verify the supposition.

2.1.2 (Maleated) epoxy asphalt binder

With the addition of 0.3% accelerant, plots of viscosity vs. time in the curing process of component B with component A, which was made up of asphalts modified with or without MAH or SAH, are presented in Fig. 2. As shown, (maleated) epoxy asphalt binders with 0.3% accelerant show good curing curves and can be cured in 4 h. This is attributed to the Diels-Alder reaction involving the active maleic anhydride double bond and the condensed aromatic ring in the bitumen, which made the asphalt into an effective curing agent

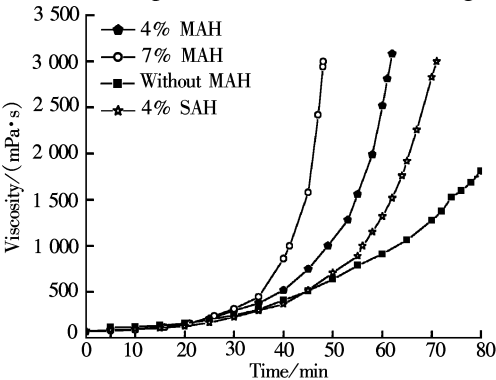


Fig. 2 Viscosity vs. time curves in the curing process of various component A with component B (120 °C)

for the epoxy resin. Further experiments were carried out to verify this hypothesis. As expected, the 4% SAH modified epoxy asphalt binder cannot be cured in 4 h (Tab. 1, sample No. 3). Fig. 3 indicates the effectiveness of accelerant on the curing curves of (maleated) epoxy asphalt.

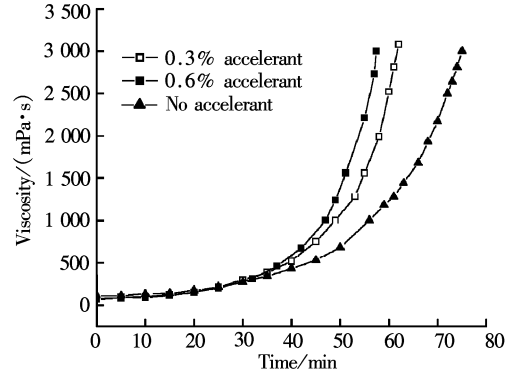


Fig. 3 Viscosity vs. time curves in the curing process of maleated epoxy asphalt with a range of accelerant concentration (120 °C)

2.1.3 Conversion of MAH

Unfortunately, we cannot determine the conversion of MAH accurately because the MAH is readily volatile at these temperatures. In principle, the end conversion increases with the increase of temperature and at last the reaction reaches equilibrium. According to Fig. 4, the optimal reaction temperature is adopted at 140 °C for 4 h.

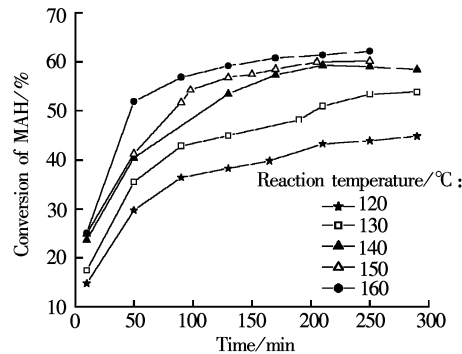


Fig. 4 Conversion of MAH during Eq. (1)

2.2 Epoxy asphalt concrete

The epoxy asphalt has been proved to be thermosetting asphalt because the samples after DTT did not melt or flow when placed onto hot plates at about 300 °C for 4 h. Furthermore, the DTT and rheological measurements indicated that the 4% MAH modified epoxy asphalt used to prepare the final binders was the best choice. Therefore, the Marshall testing was performed in order to determine the properties of the asphalt concrete.

In order to distinguish the degree of thermoset-

ting, the Marshall testing samples were separated into two categories: uncured compaction samples (see Tab. 2) to characterize the properties of newly-paved asphalt concrete and cured compaction samples (see Tab. 3) to characterize the end properties. Also, the fatigue test of combined beam was carried out by MTS[®] 810.

Tab. 2 Results of cured Marshall testing

Sample	Specimens specific gravity/($\text{g}\cdot\text{cm}^{-3}$)	Air voids/%	Stability/kN	Flow value/(0.1 mm)
No. 9	2.581 2	2.4	36.7	46.3
No. 10	2.567 8	3.0	38.4	45.5
No. 11	2.577 5	2.6	36.0	50.7
Average			37.0	47.5

Tab. 3 Results of cured Marshall testing

Sample	Specimens specific gravity/($\text{g}\cdot\text{cm}^{-3}$)	Air voids/%	Stability/kN	Flow value/(0.1 mm)
No. 12	2.578 3	1.9	10.0	29.1
No. 13	2.569 1	2.1	10.4	29.6
No. 14	2.586 4	2.2	10.3	29.0
Average			10.2	29.2

From the results shown in Tab. 3, the road paved with present epoxy asphalt binder can be exposed to traffic at once because the concrete has a little higher stability than that of SMA asphalt concrete^[24]. Furthermore, after standing at 120 °C for 4 h, the Marshall stability of the concrete is much higher than that of the just prepared specimens. Therefore, it is important to maintain it at high temperatures in order to obtain better performance. At the same time, the combined beam is still in good condition after 12×10^6 cycles load.

3 Conclusion

Based on the study in this paper, it is concluded that the curing rate, rupture elongation and the tensile strength of maleated epoxy asphalt modified by MAH have a more evident increase than those of the materials modified without MAH or using SAH, although only 50% to 60% of the MAH has reacted with the asphalt irreversibly (probably by Diels-Alder mechanism). Moreover, 4% MAH modified asphalt with other curing agents (organic acid and organic anhydride) is the best choice in preparing the epoxy asphalt. It can be controlled by means of the addition of tertiary amine accelerant to provide a proper pot life. Large elongation and good fatigue resistance of the epoxy asphalt are attributed to the formation of the infusible, insoluble thermosetting asphalt composites, which result in a relatively good paving material for the steel deck bridges, especially in hot region.

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钢箱梁桥铺装用环氧沥青材料制备和表征

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摘要:制备两组分的热固性环氧沥青,其中一个组分是顺酐化沥青、环氧树脂的固化剂和促进剂,另外一个组分是环氧树脂. 分别使用 Brookfild 粘度计、拉伸实验和 MTS 研究了沥青的铺装适用性和混凝土性能. 结果表明:尽管加入的顺酐仅有 50% ~60% 与基础沥青发生了反应,但是与未对沥青进行顺酐化比较,其固化速率、断裂延伸率和抗拉强度等都有显著的提高. 4% 顺酐改性的沥青和固化剂结合与环氧树脂固化后具有平均断裂延伸率 281. 9%, 平均强度 2. 63 MPa, 固化混凝土的 Marshall 稳定度 37. 0 kN, 未固化混凝土的 Marshall 稳定度 10. 2 kN, 耐疲劳实验 1 200 万次试件无破坏.

关键词:环氧沥青;制备;表征

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