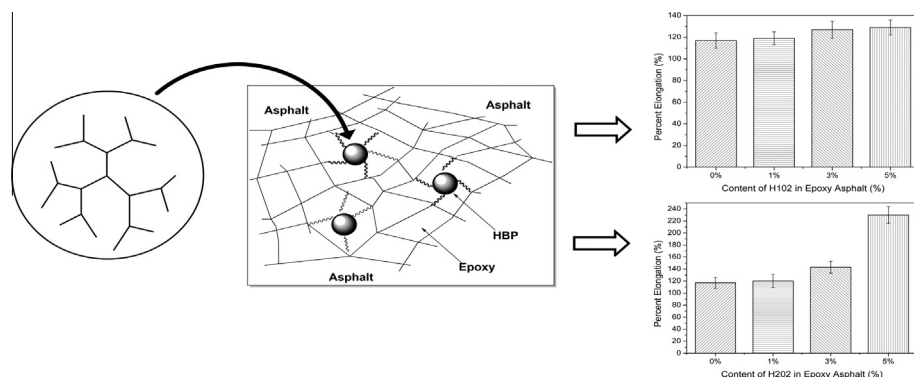


Technical note

Toughness modification of hyperbranched polyester on epoxy asphalt

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GRAPHICAL ABSTRACT



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ABSTRACT

Thermosetting epoxy asphalt, which has great mechanical properties and excellent thermal stability, is one of the preferred paving materials on steel bridge deck. However, because epoxy asphalt has high modulus and brittleness in cold environments, it still has a risk of propagating non-repaired brittle crack in winter. Hyperbranched polymer (HBP) can be used as an active modifier for epoxy asphalt to improve its toughness. It can be found that viscosities of HBP modified epoxy asphalts are slightly increased during curing process, but the percent elongation of epoxy asphalt could be effectively improved by HBP with enough tensile strength.

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1. Introduction

In the high performance paving materials, epoxy asphalt, which is different from traditional thermoplastic asphalt pavement, is an upgrade paving material for its thermosetting characteristic. It has great pavement performance, high thermal stability, rutting resistance and long service life [1,2]. However, in cold environments,

brittle crack probably propagates in the epoxy asphalt which has transformed as brittle glassy material; and the cracks in this cross-linked thermosetting epoxy asphalt would be difficult to be healed. Toughness modification is an effective method to avoid occurring the brittle fracture in epoxy asphalt at low temperature for preparing high performance paving materials.

It can be draw lessons from the modification methods of other polymers to investigate the toughness modification for epoxy asphalt. In the area of toughness modification for thermosetting resins, glassy epoxy resins are well-known inherently brittle materials which can be toughened by rubbers, thermoplastic resins or nanoparticles [3–7]. These modifiers must be initially miscible in

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the epoxy resins, but should phase-separation at some point prior to gelation so that a “sea-island” morphology is formed to initiate the toughening mechanism [8]. Unfortunately, rubbers, thermoplastic resins or nanoparticles tend to be either solids or high viscosity liquids which would cause large increase in viscosity of the final formulation with even comparatively small amounts of modifier. Poor compatibility between some toughness modifiers and matrix also results in difficult dispersion of the modifier in the matrix [9]. When it comes to epoxy asphalt, the same problems also accompanied in toughness modification of epoxy asphalt by using these traditional modification methods. Low viscosity and good compatible epoxy asphalt system is essential for epoxy asphalt mixture paving process. Therefore, novel toughness modification method for epoxy asphalt to get low viscosity, good curing processability, great compatibility and high mechanical properties are required.

Hyperbranched polyester (HBP) has highly branched structures, massive functional end groups, low solution viscosity and so on. It can be used as an active modifier for thermosetting resins to improve their processability and mechanical properties [10,11]. Compared with the conventional modifiers of thermosetting resin, HBP could improve the percent elongation and toughness of resins due to the highly branched structure and high density of surface functional groups [12,13]. Introducing HBP into thermosetting materials is an effective and significant modification method to prepare novel high performance materials [14,15]. In this paper, HBP is used to modify the thermosetting epoxy asphalt; and the modification effects of HBP on rheological and mechanical properties of epoxy asphalt are investigated.

2. Experiment

2.1. Materials

AH-90 asphalt was supplied by ESSO Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin was obtained from Wuxi Resin Factory of Bluestar New Chemical Material Co., Ltd. The curing agent was self-synthesized cyanoethylation of aliphatic diamine. H102 HBP, obtained from Suzhou HyPerT Resin Science & Technology Co., LTD, is an aliphatic hyperbranched polyester in the second generation with 12 end hydroxyl groups. H202 HBP, also obtained from Suzhou HyPerT Resin Science & Technology Co., LTD, is an aromatic hyperbranched polyester in the second generation also with 12 end hydroxyl groups.

2.2. Preparation of epoxy asphalt and HBP modified epoxy asphalt

Asphalt was heated to 165 °C in an oil-bath heating iron container until it flowed fully. Then, appropriate amounts of curing agent and epoxy resin (the ratio of curing agent to epoxy resin was 39:61 by mass) were added into the heated asphalt and stirred under 400 rpm for 5 min at 165 °C to ensure the epoxy asphalt becoming essentially homogenous (the ratio of resin system to asphalt was 35:65 by mass). Moreover, HBP modified epoxy asphalt was obtained by adding H102 or H202 into the epoxy asphalt during the preparation process. And the HBP modified epoxy asphalt containing 1, 3, 5 wt% of H102 or H202 were named as epoxy asphalt-H102-1%, epoxy asphalt-H102-3%, epoxy asphalt-H102-5%, epoxy asphalt-H202-1%, epoxy asphalt-H202-3%, epoxy asphalt-H202-5%, respectively.

The mixed epoxy asphalt and HBP modified epoxy asphalt were poured into 220 mm × 160 mm × 4 mm steel moulds and cured in an air-circulating oven at 165 °C for 2 h and 60 °C for 4 days to afford cured epoxy asphalt and HBP modified epoxy asphalt castings.

2.3. Measurements

Brookfield viscometer (Model DV-II, Brookfield Engineering Inc., USA) was used to measure the viscosity of epoxy asphalt referring to Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer (ASTM D4402). The appropriate amounts of uncured epoxy asphalt or HBP modified epoxy asphalt should be immediately poured into the sample chamber and placed into the thermo container that have been preheated to 165 °C. And then the viscosity of every epoxy asphalt or HBP modified epoxy asphalt were tested at constant 165 °C for 180 mins.

The tensile strengths and percent elongation of cured epoxy asphalt and HBP modified epoxy asphalt were tested on a universal testing machine (CMT 5105, Shenzhen SANS Test Machine Co. Ltd., China) with a tensile test method according to Standard Test Method for Tensile Properties of Plastics (ASTM D638-2014) at 23 °C and a rate of crosshead movement of 500 mm/min. The specimen dimensions were prepared as TYPE IV in ASTM D638-2014. Each reported flexural strength value was the average of six successful measurements.

The static tensile strain-stress curves of cured epoxy asphalt and HBP modified epoxy asphalts were measured by using control force mode on dynamic mechanical analysis (DMA, Q800, TA Instrument, USA) at 0 °C. The rate of crosshead movement is 1 N/min. The specimen dimensions were prepared as 20 mm × 6 mm × 1 mm. Moreover, the dynamic mechanical properties of cured epoxy asphalt and HBP modified epoxy asphalts were also carried out on Q800 DMA using a single cantilever bending mode. The strain was applied sinusoidally at a frequency of 1 Hz and the heating rate was 3 °C/min. Data acquisition and analyses of storage modulus (E') and loss modulus (E'') were recorded automatically by the system from –40 to 60 °C. The cured specimen dimensions were 35 mm × 12 mm × 3 mm.

3. Results and discussion

3.1. Rheology

H102 and H202 with hydroxyl end groups could slightly accelerates the curing rate and increases the viscosity of the epoxy asphalt, but the viscosities of H102 or H202 modified epoxy asphalt can still meet the construction requirement after 180 mins. Kevin and Donn [16] believed that the optimum viscosity range of epoxy asphalt is 2–3 Pa·s for compacting epoxy asphalt mixture. The mixture would become too hard to be compacted and to form eligible pavement surface if the viscosity of epoxy asphalt exceeds the level of 3 Pa·s. Therefore, the operation time of epoxy asphalt mixture must be controlled strictly and the compacting process must be completed before the viscosity reaches 3 Pa·s. Fortunately, epoxy asphalt prepared with our self-made curing agent has sufficiently low viscosity at 165 °C for more than 180 mins. In addition, by introducing H102 and H202, viscosities of HBP modified epoxy asphalt slightly increase without influencing the curing trends of the epoxy asphalt.

H102 can slightly promote the curing process of epoxy asphalt, but the viscosity of H102 modified epoxy asphalt is always below 1000 mPa·s within 180 mins. The viscosity developing curve of pure epoxy asphalt shows that the viscosity increases rapidly within the first 40 mins, and then increases to 475 mPa·s slowly within the last 140 mins. The trend of the viscosity curve of epoxy asphalt-H102-1% is similar to the pure epoxy asphalt during the first 100 mins. Afterwards, its viscosity faster increases to 652.5 mPa·s after 180 mins. When 3% H102 is added to epoxy asphalt, the viscosity curve is similar to pure epoxy asphalt during

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