

# Modification of alkyl group terminated hyperbranched polyester on paving epoxy asphalt

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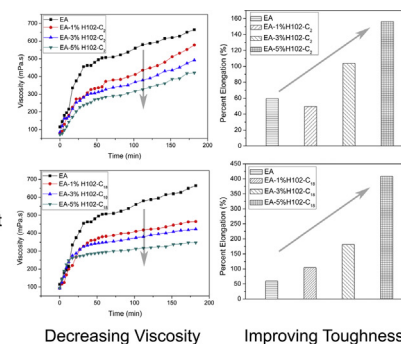
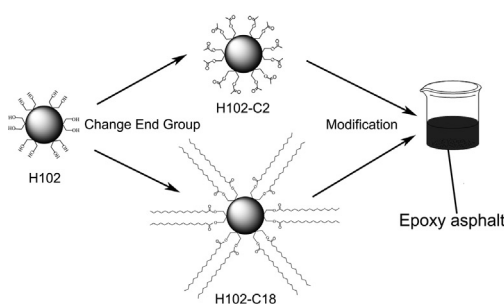
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## HIGHLIGHTS

- Active hydroxyl groups of HBP were modified as inert alkyl end groups.
- Inert H102-C<sub>2</sub> and H102-C<sub>18</sub> can decrease viscosity of epoxy asphalt during curing.
- Alkyl end groups terminated H102-C<sub>2</sub> and H102-C<sub>18</sub> can toughen the epoxy asphalt.
- H102-C<sub>2</sub> and H102-C<sub>18</sub> modified epoxy asphalt have good compatibility.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Epoxy asphalt is a kind of high performance asphalt material that has been widely used in steel deck pavement. However, because high modulus and low toughness also exist in thermosetting epoxy asphalt mixture at low temperature, crack would be initiated by innerstress caused by temperature change. Hyperbranched polyester (HBP) is a kind of toughness modifier with low viscosity and high reactivity for thermosetting materials. It can effectively improve the toughness of thermosetting epoxy asphalt. However, hydroxyl end groups of HBP would accelerate the reaction rate of epoxy asphalt and disturb the phase dispersion between resin phase and asphalt phase. Therefore, it is necessary to modify the hydroxyl end groups of HBP as inert alkyl end groups to avoid its rapid curing reaction with epoxy resin. And by this, the excellent effects of HBP, such as viscosity reduction, compatibility improvement and toughening on thermosetting materials can be obviously observed in the HBP modified epoxy asphalt. Adding different alkyl end groups modified HBP into epoxy asphalt, not only the viscosity of epoxy asphalt can be reduced, but also the toughness of cured epoxy asphalt can be improved significantly.

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## 1. Introduction

Epoxy asphalt has high strength, good deformation resistance, corrosion resistance and anti-fatigue property. It is widely used in high performance pavement. However, poor compatibility between asphalt and epoxy resin and the brittleness of epoxy asphalt at low temperature are still some tricky problems in its application [1,2]. Therefore, compatibility improvement and

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toughening modification have become the focus of epoxy asphalt investigation [3,4]. Traditionally, there are three methods may be learned to improve the compatibility and toughness of epoxy asphalt: 1). Adding natural rubber, styrene butadiene styrene block copolymers (SBS), styrene isoprene styrene block copolymers (SIS) or other elastic materials, which are easy methods to effectively improve the toughness of epoxy asphalt [5,6]. However, the viscosity of epoxy resin would be significantly increased by these viscous long-chain materials [7]. And by this method, some problems such as poor compatibility between the modifier and epoxy asphalt would also give epoxy asphalt a worse processability [8]. 2). Cis-butenedioic anhydride and maleic acid could be used to modify the asphalt to improve the toughness and compatibility of epoxy asphalt [9]. Although cis-butenedioic anhydride and other polymers can improve the viscoelastic properties of asphalt, the high viscosity and high cost of this modified asphalt may also hinder its application in epoxy asphalt [10,11]. 3). Curing agents with long-chain fatty acid or anhydride have good compatibility with epoxy resin and asphalt [12,13]. It is advantageous to bring epoxy resin into asphalt system. However, the rapid reaction between this kind of curing agent and epoxy resin would cause some harsh construction problems during the epoxy asphalt pavement. Therefore, it is necessary to develop a new method to improve the toughness of epoxy asphalt and accompanied with low viscosity, good compatibility and high enough strength.

Hyperbranched polyester (HBP) has highly branched structures, many functional end groups, low viscosity and so on [14]. It has been widely used in the modification of epoxy resin to improve their processability and mechanical properties [15,16]. Xu et al. [17] found that the mechanical properties and compatibility of epoxy asphalt also can be improved by introducing a little of HBP into the epoxy asphalt [18]. However, because many hydroxyl end groups of HBP have high reaction activity with epoxy resin, the viscosity of epoxy asphalt during curing process could be increased by HBP [19,20]. If the hydroxyl end groups of HBP can be modified as inert groups. The reaction between HBP and epoxy resin can be avoided; and the viscosity of epoxy asphalt also can be decreased by this inert HBP [21,22]. Alkyl groups are good choice for modifying the hydroxyl groups of HBP. In this paper, we choose acetyl chloride and long-chain alkyl chloride to modify hydroxyl groups on HBP [23,24]. The acetyl chloride is an easily obtained material for preparing short-chain alkyl group terminated HBP to decrease the reactivity of HBP. Furthermore, in order to improve the compatibility of HBP between asphalt and epoxy resin system, long-chain alkyl group which structure is familiar with asphalt and curing agent are also chosen as end groups of HBP [25,26]. Therefore, stearic acid chloride is used to modify the HBP and help HBP to improve the toughness and compatibility of epoxy asphalt. By introducing the short-chain or long-chain alkyl end groups terminated HBP, the effect of compatibility and toughness of modified epoxy asphalt are investigated.

## 2. Experiment

### 2.1. Materials

H102, obtained from Wuhan HyPerbranched Polymer Resin Science & Technology Co., Ltd, is an aliphatic hyperbranched polyester in the second generation with 12 end hydroxyl groups. N,N-Dimethylformamide (DMF), dichloromethane, triethylamine, anhydride, phenolphthalein, acetone and pyridine were obtained from Tianjing Tianli Chemical Reagents Co., Ltd. Acetyl chloride and stearic acid were purchased from Tianjing Fuchen Chemical Reagents Co., Ltd. Thionyl chloride, sodium hydroxide, hydrochloric acid (HCl) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were supplied

by Tianjing Bodi Chemical & Industry Co., Ltd. SK-90 asphalt was supplied by SK Holdings 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 supplied by Shaanxi Aipuke New Material Technology Co., Ltd.

### 2.2. Preparation of alkyl terminated HBP

#### 2.2.1. Synthesis of acetyl end groups terminated H102

0.02 mol of H102 and 0.29 mol of acetyl chloride were mixed together in acetone at 0 °C and poured into a three mouth flask. The reaction occurred at room temperature with stirring for 10 h in the presence of triethylamine (acetone and triethylamine volume ratio is 2.5:1) as catalyst (Scheme 1). After reaction, the acetone was removed by vacuum distillation at 57 °C; and the resultant material was dissolved in 75 mL dichloromethane. The solution was washed twice with 60 mL HCl (1 mL/L), 60 mL 10%  $\text{NaHCO}_3$  solution and separated with the pear-shaped separatory funnel, respectively. Then, removing dichloromethane and water by vacuum distillation at 40 °C. Finally, the acetyl end groups terminated H102 (H102-C<sub>2</sub>) was obtained after drying in the vacuum oven at 40 °C for 24 h.

#### 2.2.2. Synthesis of fatty alkyl end groups terminated H102

75.11 g (0.26 mol) stearic acid was added into a three mouth flask with condenser, thermometer and stirrer. Then, 43.99 g (0.37 mol) thionyl chloride was added into the flask by constant pressure dropping funnel. And adding 8–9 drops of DMF catalyzer into the stearic acid reaction system. After 2.5 h of reaction at 70 °C, thionyl chloride was separated by vacuum distillation under the temperature of 80 °C. The finally obtained yellow transparent liquid is fatty acyl chloride (C<sub>18</sub>).

Fatty alkyl end groups terminated H102 (H102-C<sub>18</sub>) was synthesized by H102 (0.02 mol) and C<sub>18</sub> (0.22 mol) in acetone with the presence of triethylamine (acetone and triethylamine volume ratio is 2.5:1) as catalyst (Scheme 2). After reaction at room temperature for 10 h, the solvent was removed by vacuum distillation at 57 °C; and the resultant material was dissolved in 75 mL dichloromethane. The solution was washed twice with 60 mL HCl (1 mL/L), 60 mL 10%  $\text{NaHCO}_3$  solution and separated with the pear-shaped separatory funnel, respectively. Then, removing dichloromethane and water by vacuum distillation at 40 °C. Finally, H102-C<sub>18</sub> was obtained after drying in the vacuum oven at 40 °C for 24 h.

### 2.3. Preparation of epoxy asphalt and HBP modified epoxy asphalt castings

A certain amount of curing agent and epoxy resin (the ratio of curing agent to epoxy resin is 39:61 by mass) were added into the asphalt (the ratio of resin system to asphalt is 35:65 by mass) and stirred at 165 °C by high speed of 800 r/min for 5 min to insure the epoxy asphalt (EA) uniformly mixed. HBP modified EA was obtained by adding 1, 3, 5 wt% H102-C<sub>2</sub> or H102-C<sub>18</sub> into the EA during its preparation process. And the HBP modified EA were named as EA-1%H102-C<sub>2</sub>, EA-3%H102-C<sub>2</sub>, EA-5%H102-C<sub>2</sub>, EA-1%H102-C<sub>18</sub>, EA-3%H102-C<sub>18</sub>, EA-5%H102-C<sub>18</sub>, respectively. Pouring the prepared HBP modified EA into a 240 mm × 160 mm × 4mm aluminum flat molding and curing at 165 °C for 2 h and at 60 °C for 4 days in oven. And the cured EA and HBP modified EA castings were obtained.

### 2.4. Measurements

#### 2.4.1. Hydroxyl value titration

The residual hydroxyl groups on the H102-C<sub>2</sub> or H102-C<sub>18</sub> samples can react with the anhydride to form carboxylic acid. And the

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