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# Influence of freeze–thaw cycles on properties of asphalt-modified epoxy repair materials

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## HIGHLIGHTS

- The epoxy repair materials have excellent freeze–thaw resistance and mechanical property.
- The mechanical property further increases upon the freeze–thaw circles.
- The repair materials have a “sea island structure”.
- The materials have the outstanding water and chemical resistance.

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## ABSTRACT

A high performance repair materials for concrete is prepared using epoxy resin as a base resin and asphalt as a modifier, respectively. The influence of the asphalt content, freeze–thaw circles, and chemicals on the structure and properties of the repair materials is investigated in detail in this work. Results show that the epoxy repair materials modified with 10 phr of asphalt has the excellent mechanical property, and the compressive strength and tensile shear strength can reach 56.6 MPa and 5.9 MPa, respectively. The compressive strength further increases while the weight change for all samples is below 1 wt% when the repair materials suffer 30 freeze–thaw circles and chemicals soakage at 80 °C for 2 weeks, indicating that the asphalt-modified epoxy repair materials have the outstanding water, acid, and alkaline resistance and salt tolerance. Therefore, a kind of asphalt-modified epoxy repair materials with excellent freeze–thaw resistance is developed in this research.

## 1. Introduction

Concrete is one of the most versatile construction materials and is the material which is the most consumed besides water worldwide [1]. Not only for it possesses high compressive strength, but it is relatively inexpensive, durable, strong, and can be molded into any shape. However, concrete, the multiphase heterogeneous brittle material, presents low tensile strength and bad toughness. As a result, cracks may develop due to the combined effects of overloading, drying shrinkage, temperature variations, chemical attacks [2], weathering, freeze–thaw cycles, differential settlement and other degradation processes [3,4]. Cracks in concrete are not only harmful to outward appearance after cracks appears on concrete structure and makes us feel unsafe, but the main reason for a decreased service life, especially the durability of concrete structures. Sometimes, even a destructive omen will lead to grave consequence [5].

In the arcticalpine and highland areas of China, especially in the northeast, northwest, North China and etc., with the effect of the various natural factors, such as low temperature, big differences in temperature, drying and watering cycle, freeze–thaw cycle, salt alkaline corrode, and wind erosion. In cold-weather coastal regions, the main concern for durability of the adhesive bond between the base materials is resistance to freeze–thaw cycles [6]. Almost 100% projects, local or large areas, suffers varying degrees of freeze–thaw destroy (main disease is denudation, cracks and etc.) [7,8], even some projects were discovered grave freeze injury during construction right away or before long after construction process is completed. Freeze–thaw destroy seriously affected the durability of concrete [9,10].

The repair of concrete structure cracks has been paid more and more importance over the past few years, which is because reduction in the service-life of concrete construction is a major problem that confronts the construction industry worldwide. Repair and

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rehabilitation of cracking concrete structures are extremely important not only to make use of their intended service-life, but also to assure the safety and applicability of the related components [11]. Therefore, it is very important for ensuring the durability of concrete structure by timely investigating, seeking the causes, and taking appropriate materials and technology for repairing. In recent years, the polymer alloy has already become an indispensable kind of repair material in the concrete crack repairing field. Several repair materials, such as epoxy resins, polyester resins, polymer latexes, and polyvinyl acetates, are used for repairing cracking concrete structures. Of various polymer matrix repair materials, epoxy resin (EP) materials with good mechanical, electrical and thermal properties have been widely used in many fields including mechanical engineering, chemical engineering, and electrical/electronic engineering, as well as aviation and aerospace industry [12–16]. The practical use of EP coatings in industry, however, is seriously limited by poor impact resistance and cracking resistance. To overcome this drawback, researchers have made numerous attempts to modify epoxy resin by introducing various reinforcing and toughening agents and fillers [17,18], such as rubbers and asphalt [19,20].

At the same time, grounded on the advantage of the high and subzero temperature properties, a better mechanical performance, a better stability at high temperature, and a better cracking resistance at lower temperature [21–23], the asphalt is also widely used to repair the concrete structure cracks. Combining the merits of epoxy resin and asphalt, the epoxy asphalt is developed and used in the field of the crack repairing. However, previous researches have focused on the viscosity to control construction time [24], while there were few reports about the asphalt-modified epoxy resin, and the influence law of the toughening agent of asphalt on the properties of the repair materials suffered from freeze–thaw cycles, and which is very important for the repair materials used in the arcticalpine, drought and marine environments, dominated by extremely low temperature, high aridity, salt, acid, and alkali. In this article, a high performance repair materials for concrete is prepared using epoxy resin as a base resin and asphalt as a toughening agent, respectively. The influence law of the asphalt content on the properties and structure of the epoxy repair materials suffered freeze–thaw cycle and chemicals is investigated through using interior freeze–thaw circulating experiment, which will provide theoretical basis and practice for further optimizing the repair materials and the application in the arcticalpine and drought environments.

## 2. Materials and methods

### 2.1. Materials

E-44, one of a bisphenol-A epoxy resin (epoxy value: 0.41–0.47 mol/100 g, and $M_w$: 425–490 g/mol), was supplied by Wuxi Resin Factory (China). Curing agent F, a modified fatty amine, was prepared in our lab. Asphalt, 70-A (needle penetration (25 °C, 100 g, 5 s): 60–80 × 0.1 mm, penetration index (PI): $-1.5 \sim +1.0$, softening point (ring and ball method): 42–52 °C, flashing point: no less than 260 °C), was purchased from Qilu Company (Sinopec Group). Sulfuric acid and hydrochloric acid, analytical reagents (AR), were provided by Sinopharm Group Chemical Reagent Co., Ltd. (China). Sodium chloride and sodium hydroxide, analytical reagents (AR), were supplied by Shanghai Boer Chemical Reagent Co., Ltd. (China).

### 2.2. Preparation of the epoxy repair materials

Asphalt was heated to 120 °C until it flowed fully. Then, 0, 10, 20, 30 phr of asphalt (phr presents the weight ratio of agent to 100 g of epoxy resin) was introduced into the epoxy resin under stiring for about 30 min to ensure the blend becoming essentially homogenous, respectively. When the temperature of the epoxy resin/asphalt mixture was reduced to room temperature, 15 phr of curing agent was added into the blend and mixed for 30 min to create an essential homogeneity. Finally, the mixture was poured into models to prepare the asphalt-modified epoxy repair materials samples, and the samples were maintained at room temperature for 2 weeks before characterization.

### 2.3. Procedure of the freeze–thaw circles

The freeze–thaw experiment was carried out by repeating the freezing and thaw circle according to the scheduled procedure (ICBO 2001) [6]. The samples of epoxy repair materials were immerged into the tap water in plastic bottles, and then a repeatable daily schedule (i.e., 24 h cycle) was adopted as follows: 14 h in the freezer, 4 h deicing in 100% relative humidity chamber, and 6 h in the oven for drying. The temperature of deicing and drying was both set to 50 °C while that of the freezer was set to −20 °C. After the daily schedule, the next freeze–thaw cycle came on. The freeze–thaw experiment was repeated for 10, 20, and 30 cycles, respectively. Then the compressive strength, water and chemical resistance of the repair materials were evaluated.

### 2.4. Characterization

#### 2.4.1. Fourier transform infrared spectroscopy (FT-IR) analysis

Fourier transform infrared spectra were performed on a FTS-3000 Spectrometer (DIGILAB Company, America) using KBr pellet technique. Absorption spectra were saved from 4000 to 400 $cm^{-1}$.

#### 2.4.2. Tensile shear strength measurement

Tensile shear strength measurement of samples with dimensions of 100 mm × 25 mm × 12.5 mm was carried out using the AG-10kN universal testing machine (SHIMADAZU Company, Japan) based on China National Standard of GB/T 7124-2008. The loading rate was 5 mm $min^{-1}$.

#### 2.4.3. Compressive strength measurement

Compression tests were conducted on sample with dimensions of 20 mm × 20 mm × 40 mm using the YE-30 testing machine (Jinan testing company, China) according to China National Standard of GB/T 2567-2008 in order to determine the compressive strength of the composites.

#### 2.4.4. Water resistance evaluation

The water resistance of repair materials was evaluated by scaling the weight change before and after freeze–thaw circles. The ratio of weight change (WC) of the repair materials is calculated using the following equation:

$$WC\ \% = \left|\frac{m - m_0}{m_0}\right| \times 100\% \tag{1}$$

where $m_0$ presents the weight of the repair materials before freeze–thaw circles, and m denotes the weight of the repair materials after freeze–thaw circles.

#### 2.4.5. Chemical resistance test

The chemical resistance of repair materials after freeze–thaw circles was investigated with 10 wt% of $H_2SO_4$, 10 wt% of NaOH, and 10 wt% of NaCl, respectively according to China National Standard of GB/T 2567-2008. The repair materials before and after freeze–thaw were soaked in each chemical solution at the temperature of 80 °C for 2 weeks. The ratio of weight change of the repair materials before and after soakage was used to evaluate the chemical resistance.

#### 2.4.6. Scanning electron microscopy (SEM) observation

To better understand the effect of the asphalt as well as freeze–thaw on the repair materials, the morphology of the sample fracture was observed with a scanning electron microscope instrument (SSX-500, Shimadzu). Before observation, the fracture surfaces were sputter-coated a thin layer of gold to make them electrically conductive.

## 3. Results and discussion

### 3.1. Chemical structure of asphalt-modified epoxy repair materials

Fig. 1 shows the FT-IR spectra of asphalt-modified epoxy resin before and after cured. Fig. 1a is the FT-IR spectrum of asphalt (10 phr) modified epoxy resin before cured. The appearance of a band centered at 3450 $cm^{-1}$ is attributed to the stretching signal of the hydroxyl groups. 2925 $cm^{-1}$ and 2855 $cm^{-1}$ are the telescopic vibration absorption of methyl and methylene groups. Meanwhile, the strong bands at 835 $cm^{-1}$, 1510 $cm^{-1}$ and 1615 $cm^{-1}$ are due to the absorption of p-phenylene groups, and the peak at 1035 $cm^{-1}$ results from the aliphatic carbon–oxygen stretching ($-O-CH_2-$). More importantly, it can be found that there is a distinct absorption peak at 910 $cm^{-1}$ which is assigned to the characteristic absorption of epoxy groups [18,25,26]. By contrast, this absorption peak almost disappears after the asphalt-modified