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# Surface modification of crumb rubber and its influence on the mechanical properties of rubber-cement concrete

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## HIGHLIGHTS

- Oxidation and sulphonation introduced strong polarity groups to crumb rubber surface.
- The surface modification generated a strong chemical bond between rubber and cement matrix.
- The mechanical properties of rubber concrete were improved due to the surface modification.

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## ABSTRACT

In this paper, a surface modification method was proposed to introduce strong polarity groups to rubber surface to generate a strong chemical bond between the rubber and the cement matrix. Rubber was first oxidized with $KMnO_4$ solution and then sulphonated with $NaHSO_3$ solution. The Fourier transform-infrared (FT-IR) spectra and contact angle measurement showed that the oxidation and sulphonation process introduced a large number of hydrophilic hydroxyl and sulfonate to crumb rubber and decreased the contact angle between rubber surface and water, thus greatly improved the interfacial bonding strength between crumb rubber and cement paste. After the rubber surface modification, the adhesion strength of the rubber and cement paste was increased by 41.1%. It was also found in the mechanical tests that the rubber surface modification was quite useful to enhance the compressive strength and impact strength of rubber-cement concrete. The compressive strength of the concrete with 4% modified rubber powder was 48.7% higher than that with ordinary rubber powder. Based on the results, it is concluded that the surface modification of crumb rubber with $KMnO_4$ and $NaHSO_3$ solutions is an effective method to improve the mechanical properties of rubber-cement concrete.

## 1. Introduction

With the rapid development of modern transportation and manufacturing industry, a great amount of scrap rubber is produced. The treatment and comprehensive utilization of waste tire and rubber products are highly concerned. Currently, the produced crumb rubber powder is widely used to incorporate organic or inorganic composite materials [1]. Concrete mixed with crumb rubber has better toughness and impact strength than ordinary concrete, and also has better heat insulation and sound insulation properties [2–4]. However, crumb rubber has bad interface compatibility with inorganic materials. Cement paste is a hydrophilic material, while the surface of crumb rubber is hydrophobic. Thus, the adhesion between crumb rubber and cement paste is poor, impairing the mechanical properties of the rubber cement matrix material and limiting the development and application of rubber cement based products.

In recent years, a lot of research has been done to enhance the performance of rubber-modified concrete through surface treatment of crumb rubber. Mohammadi et al. evaluated the performance of rubberized concrete prepared with sodium hydroxide (NaOH) treated rubber and found that this treatment method resulted in notable improvement of the compressive strength and moderate enhancement in the flexural strength, but did not lead to better adhesion characteristics of the rubberised concrete for all treatment methods used due to the rougher surfaces of the modified rubber particles [5]. Segre et al. indicated the main role of NaOH is to remove the tire rubber soaked formulation additives and saturated in NaOH solution for 24 h did not change the

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hydrophobic nature of rubber, with water contact angle of the rubber surface still higher than 90° [6]. Zhang et al. treated the rubber particles with acrylic acid (ACA) and polyethylene glycol (PEG) for grafting hydrophilic groups on their surfaces and found that the slump, air-entrainment, compressive strength, flexural strength, and impact performance of modified rubberized concrete were obviously improved [7]. Onuaguluchi investigated the efficiency of a two-stage approach of using limestone powder (LP) pre-coated crumb rubber and silica fume (SF) to enhance the performance of rubberized cement mortar and found that higher flexural strength were obtained in mixtures containing SF and up to 10% LP pre-coated crumb rubber [8]. Rivas-Vázquez et al. treated the rubber fibers surface with different solvents to improve adhesion of the rubber fibers to the concrete matrix and observed that the tire rubber treatment with acetone caused an increase of the mechanical strength of the samples [9]. Gupta et al. studied the performance of concrete with rubber fibers (obtained by grinding waste rubber tires) as partial replacement of fine aggregates and found that silica fume enhances the strength and durability properties of rubberized concrete [10]. Ossola and Wojcik studied the effect of surface-treating rubber crumb (obtained from discarded tires) with ultraviolet (UV) radiation and found that exposure to UV was beneficial to flexural strength of the cementitious composites [11]. Dong et al. have reported varying degrees of success of surface treatment through increasing the rubber surface polarity [12]. Yang et al. reported that the acidic potassium permanganate oxidation of rubber can improve the strength of rubberized concrete [13]. After surface oxidation, the surface polarity of rubber increased with the increase of oxygen groups. However, there are only partial hydrogen bonds and intermolecular forces between the groups and the cement matrix, and difference in energy still exists between the rubber surface and the strong polar cement matrix. This paper intends to introduce strong polarity groups to the rubber surface, so that a strong chemical bond between the rubber and the cement matrix can be generated. In such a way, the interface bonding properties between rubber and cement matrix will be enhanced and the mechanical strength of rubber-cement concrete be improved.

## 2. Experimental

### 2.1. Materials

The scrap rubber used in this research is tire crumb rubber (40 mesh, with an apparent density of 1.1 g/cm$^3$) and tire inner tube block. The analytical reagents used to modify rubber include sodium hydroxide solution, 5% solution of potassium permanganate, sulfuric acid and saturated sodium bisulfite solution. The cement used was early strength ordinary Portland cement of 42.5R. The tenuous sand used was ordinary river sand with an apparent density of 2.7 g/cm$^3$. The gravel has an apparent density of 2.65 g/cm$^3$. The water-reducing agent used can reduce the volume of water needed by 10%.

### 2.2. Rubber modification

The flowchart of the rubber modification process is shown in Fig. 1.

Crumb rubber (block) was firstly soaked in 5% NaOH solution for 24 h, and then rinsed in clear water. Secondly, crumb rubber was added into 5% $KMnO_4$ solution and the pH value of this solution was adjusted to 2–3 by adding sulfuric acid. Thirdly, the solution was heated to 60 °C and stirred to allow the oxidation reaction for about 2 h. The pH value of solution was maintained 2–3 during this process by adding potassium permanganate solution and sulfuric acid. After the oxidation, the crumb rubber powder or block was rinsed in clear water and soaked in saturated sodium bisulfite solution at 60 °C for 0.5–1 h to complete the sulphonation reaction of the rubber.

### 2.3. FT-IR characterization of rubber surface

The FI-IR characterization was used to analyze the change of functional groups at the rubber surface after modification. This test was performed with a Spectrum 100 FT-IR, PerkinElmer, USA. Raw rubber or modified rubber particles were grinded together with potassium bromide and compressed into tablets for FI-IT testing.

### 2.4. Contact angle test

The change of the polarity at the rubber surface due to modification was examined by contact angle between water and the surface of rubber with a HARKE-SPCA, Video Optical Contact angle Measurement (Hake Test Instrument, Beijing). The contact angles of five pieces of the original and modified tire inner tube blocks were measured respectively. Removing the maximum and the minimum value for each group, the remaining three values were used to calculate the average contact angle of the samples.

### 2.5. Adhesive strength test

The adhesive strength between rubber and cement is closely related to their interaction at the interface. In this paper, the adhesive strength was used to evaluate the effectiveness of surface modification of rubber.

#### 2.5.1. Specimen preparation

The original and modified tire inner tube blocks were cut into small pieces with the size of about 20 mm × 20 mm × 6 mm (the adhesive area is calculated on the basis of actual measurement). Cement paste was prepared with ordinary portland cement of 42.5R MPa grade and a water cement ratio 0.4 modulation. Then, the cement paste of 1 mm thick was set on a brick (200 mm × 100 mm), which soaked in water overnight in advance, then removed, wipe the surface of the water to a saturated surface dry state. Five pieces of each kind of rubber block were evenly placed on the cement paste (as shown in Fig. 2). The brick was cured for 28 days at 20 °C with a humidity of 100% before measuring the adhesive strength between the rubber blocks and the cement paste.

#### 2.5.2. Adhesive strength test

A self-made test device (shown in Fig. 3) was used to measure the adhesive strength between the rubbers and cement paste. In Fig. 3, carrying bricks of the specimen is fixed on a platform and the rubber block was tied on a wire which was connected with a barrel. Rocks and fine sand were slowly added to the barrel until the rubber block was pulled out of the cement paste. The adhesive strength between the rubber and cement paste can be calculated according to formula (1).

$$R = mg/A \tag{1}$$

where R is adhesive strength (MPa), m is the weight of the barrel (including gravel) (kg), g is the gravitational acceleration, A is the contact area between the rubber block and the cement paste (mm$^2$).

Five adhesive strength data were obtained for each group of rubber. Removing the maximum and the minimum value from each group, the remaining three values were used to calculate the average adhesive strength of the samples.

### 2.6. Compressive strength test

Concrete was mixed with cement: sand: stone chips: gravel ratio 1:0.65:0.85:3.04, water-cement ratio 0.46, water reducer content 0.3%, and rubber powder content 2%, 4%, 6% (mass percent of the concrete). When adding rubber powder, some sand with the same volume of rubber was replaced. Cubic concrete specimens with dimension 100 mm × 100 mm × 100 mm were prepared and cured in the standard curing conditions for 28 days before testing the compressive strength.

### 2.7. Impact resistance test

The concrete specimens after 28 days' curing were cut in half and used for impact resistance test, which was to use a Marshall Compactors to simulate the drop-weight test of resistance impact in ACI 544.2 R. The compactor has a hammer

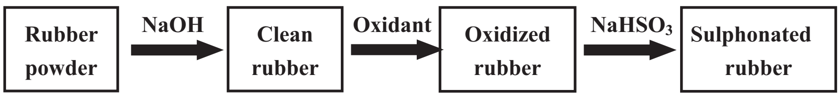

**Fig. 1.** Flowchart of the rubber modification process.