

Improvement of the Properties of Plasma-Modified Ground Tire Rubber-Filled Cement Paste

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ABSTRACT: The thesis investigated that the adhesion of ground tire rubber (GTR) to cement can be improved by applying surface plasma modification. The hydrophobic surface of GTR powder has been transformed to a hydrophilic one through plasma treatment. Attenuated total reflectance Fourier transform infrared spectral studies showed the increase in peak intensity at the range of 1400–1600 cm^{-1} , indicating the generation of carbon–carbon double bond after plasma treatment on the surface of the GTR powder. The X-ray photoelectron spectroscopic analysis further confirmed the presence of oxygen-containing polar functional groups on the surface of the GTR powder after atmospheric plasma treatment. The improve-

ments in plastic deformation and elastic deformation that attributed to the enhanced interfacial interaction between modified GTR powder and cement matrix were observed for the modified GTR-filled cement paste via triaxial test. The pore size distribution testing manifested a better compactness of plasma GTR-filled cement paste. Besides, scanning electron microscope illustrated that adhesion of modified GTR powder with cement matrix increased. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: plasma modification; GTR powder; cement slurry; compatibility

INTRODUCTION

Ground tire rubber (GTR), originated from used rubber products, is a kind of solid wastes. Nowadays, a large quantity of waste tires, rubber products, and scrap increase with the development of rubber and vehicle industries. Therefore, the recycling of rubber scrap has been paid more attention. The GTR scrap was treated by ground accumulation, landfilling, and incineration traditionally. That is prone to cause severe environment problems because GTR cannot be degraded, hydrolyzed, or decomposed through methods of natural biology. Accumulation of GTR may also cause safety problems such as fire hazard and mosquito breeding.¹ Moreover, there may not

be enough land for the accumulation with the rapid growth of waste tires.

In recent years, numerous studies have shown that the addition of shattered waste tire in polymer and concrete matrix makes rubberized polymer and rubberized concrete. That was a better method of recycling waste GTR.

Bignozzi et al.^{2–4} examined the characteristics of tire rubber-containing concrete, which is partially substituted by untreated tire rubber. Different categories of tires were used: scrap tires,² chipped tires,^{3,4} crumb rubber,^{2,4} and ground rubber.³ However, regardless of the different nature, size, and composition of the tire rubbers, the concrete compressive strength decreased with the increasing percentage of rubber replacement in the mixture.

Otherwise, the tensile strength of concrete also reduced. The most important reason is a lack of proper bonding between the rubber and the paste matrix owing to the crosslinked structure and surface characteristics of the tire rubber. It is necessary to adopt the surface modification for improving adhesion between the two phases.

Cañavate et al.⁵ vulcanized GTR by a new peroxide, and then mixed with high-density polyethylene (HDPE) and ethylene–propylene–diene monomer (EPDM) rubber in a suitable proportion to obtain Thermoplastic Vulcanizates. Li et al.⁶ conducted a similar investigation by modifying HDPE/scrap rubber powder composites with EPDM, dicumyl

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peroxide, and silicone oil. Both cases showed that the modified rubber composite has a better mechanical property and adhesion. Lee et al.^{7–11} mixed the modified rubber with polypropylene, HDPE, etc., to make composite. Methods of modification varied from chemical treatment, ozone treatment, ultrasonic treatment to ultraviolet treatment, and so on. Compared with the untreated composite, the tensile strength of sample further increased through ozone treatment and chemical treatment (H_2SO_4 and HNO_3) that improved the ability of rubber to interact with the HDPE. Furthermore, the compound treatment on the surface of rubber powder could give a better tensile strength than that given by the single treatment.

Yue et al.¹² adopted eight interfacial modifiers to improve interfacial bonding strength between the crumb rubber and the matrix of Crumb Rubber Mortar. According to the investigation, the interfacial bonding strength increased greatly, especially the bonding strength treated by silicone modified styrene–acrylate–emulsion. Ligang et al.¹³ added two kinds of hybrid-modified GTR powder (TRP and ATRP) modified by the sol–gel method to cement mortar. Based on the research and analysis, it was found that the nano Si–O–Si network generated in the crosslinked structure of TRP and ATRP networks. The hydrophilic group grafted on the surface of ATRP. Comparing to the mortars with unmodified GTR powders and other treated rubber powders, the rubber-treated mortar modified by the ATRP has the highest compressive and flexural strength. Eldin and Senouci¹⁴ modified GTR powder with water immersion to remove surface impurity. It was found that the compressive strength of modified GTR-filled concrete was increased by 16% than the untreated one. In addition, Chung et al.^{15–17} also adopted different methods to modify GTR powder as a partial substitute of fine aggregates in concrete to improve the mechanical properties.

Plasma surface modification, which has advantages of simple operation, no pollution to environment, and power consumption, is widely used to improve the hydrophilicity of rubber powder.^{18–20} By the low-temperature treatment, some physical and chemical changes, such as etching to produce crosslinked layer or polar group, occur on the surface of polymer material. That improves the hydrophilicity, cohesiveness, and other properties of materials. Moreover, the plasma treatment only acts on the polymer surface (usually, 50–100 Å) without affecting the properties of matrix. A X-ray photoelectron spectroscopic (XPS) analysis was conducted by Zhang et al.¹⁸ to investigate the element content variations on oxygen plasma-treated GTR powder surface. It detects that oxygen element content increases on GTR powder surface, oxygen-containing

groups (C=O and C–O) exist on the surface of the GTR powder after atmospheric plasma treatment. Yan et al.¹⁹ investigated the structure and properties of plasma-treated scrap rubber powder (SRP)/polyvinyl chloride (PVC) composite. The good mechanical properties of composite were obtained via 2-min oxygen plasma modification. Besides, the scanning electron microscope (SEM), results showed that SRP was pulled out from the PVC matrix in the untreated SRP/PVC composites. In contrast, the SRP was broken in the plasma-treated SRP/PVC composites.

However, modified GTR powder is usually used to improve the cohesiveness with organic materials. Few applications about the binding with inorganic materials such as cement are reported. In this research, the plasma surface treatment was adopted to modify GTR powder. The modified GTR surface was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometer, XPS, mercury porosimeter, and SEM. Furthermore, modified GTR powder was added to cement matrix to investigate its influences on compound materials.

EXPERIMENTAL

Materials

G class high sulfate-resistant oil well cement was purchased from Sichuan Jiahua Enterprise (Group), China. The GTR powder used in this study was produced by Sichuan Hailian Environmental Protection Technology, Hong Kong. The average particle size of the raw GTR powder is 120 μ . Other additives including lightening admixture microsilica, filtrate reducer G33S, dispersant SXY-2, tackifier HEC, defoamer Dimethicone, and defoamer Tributyl Phosphate were obtained commercially.

Plasma modification of GTR powder

The surface modification of GTR powder was carried out by using a plasma surface treatment apparatus (model DT-03 Suzhou OPS Plasma Technology, China). The raw GTR powder specimen was placed into glassware evenly, positioned in plasma treatment apparatus chamber. The vacuum pump was closed until the vacuum is <10 Pa, turned on the flow valve to let the air in. While the flow quantity equaled to the set value, turning on the high-frequency generator for a 180-s modification.

Surface characterizations

ATR-FTIR measurement

ATR-FTIR measurements of modified GTR powder were performed by using a NICOLET 560 spectrometer (USA) to investigate the details of structure

and functional group changes. The plasma-modified GTR powders were made into 0.1-mm thick GTR films by hot-pressing between two pieces of aluminum foil (180°C and 10 MPa). The spectra were collected from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} over 20 scans.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra were recorded on an XPS spectrometer (XSAM800, KRATOS, England) with a monochromatized Al K α X-ray source for a further analysis of surface group changes of modified GTR powder. Binding energies were corrected to the carbon 1 s peak located at 285.0 eV.

Preparation of modified GTR powder-filled cement pastes

Pure cement slurry was prepared with water, G class cement, filtrate reducer, dispersant, tackifier, defoamer, and lightening admixture. Performance tests were conducted according to API-10 specification to ensure the pure slurry a appropriate flowability (18–24 cm), consistency, settlement of stability, and filtration properties (the fluid loss <10 mL, the filter cake thickness <1 cm). Then, the modified GTR powders were added into the prepared cement slurry and stirred uniformly. Finally, pour the modified GTR powder-filled cement slurry into mold for curing in a water bath.

Determination of pore size distribution

The pore size distribution of cement paste was tested by a mercury porosimeter (AutoPoreIV9500, Micromeritics Instrument, Norcross, GA). First, the samples was broken into millimeter level pieces and soaked in absolute ethyl alcohol. Then, the samples were dried under the condition of drying temperature 90°C for 4–5 h.

Determination of mechanical properties

The 48-h curing of cement slurry was conducted in 90°C water bath to form the cylindrical sample with $\Phi 1 \text{ in.} \times 2 \text{ in.}$ Then, the multicycle constant speed loading test of triaxial stress was conducted by triaxial rock mechanics testing system on the conditions of triaxial (confining pressure, 16 MPa) and constant speed loading (2 kN/min). Besides, maximum cyclic loading of 20 kN was applied.

Morphology observation

SEM (JEOL JSM-5600, Japan) was used to observe the state of the adhesion performance between

plasma-modified GTR powder and cement matrix. The samples were obtained by broken bending samples, and the fractured ends of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Hydrophilic property

Figure 1 shows the dispersing stability of unmodified GTR and plasma-treated GTR (with the treatment time of 120 s) in water. It is obvious that the unmodified GTR powder cannot be well dispersed in water owing to its hydrophobic property [Fig. 1(a)]. However, the plasma-modified GTR powder evenly dispersing in water reveals a well hydrophilicity [Fig. 1(b)]. Consequently, it infers that the plasma treatment evidently enhances rubber powder hydrophilicity.

Characterization by ATR-FTIR

Figure 2 shows the structure and functional group changes of the GTR before and after the plasma treatment. Obviously, significant differences in the ATR-FTIR spectra were observed in the regions from 1400 to 1600 cm^{-1} which correspond to the carbon-



Figure 1 The dispersing stability of unmodified and plasma-treated GTR in water.

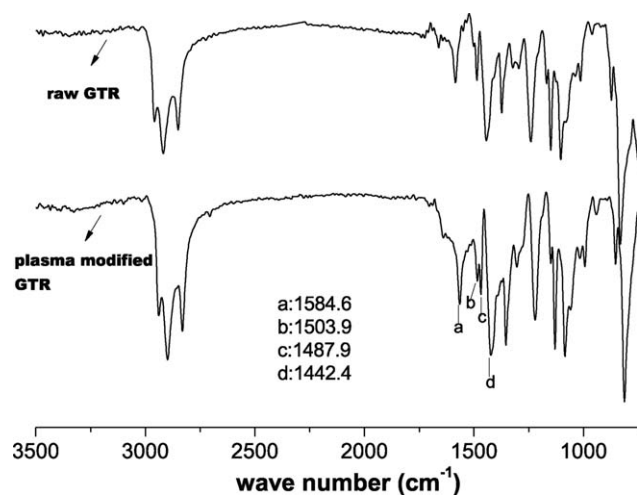


Figure 2 ATR-FTIR contrast spectrum of raw rubber powder and plasma-treated GTR powder.

carbon double bond (C=C). The intensity of these peaks shows sharp increase after the plasma treatment. This change may be attributed to the bombardment of electrons and ions that originated from ionized air during the process of plasma treatment. Then breakage of C=H bond was caused and a polymer radical was generated there. Eventually, the adjacent dehydrogenated carbon atoms formed the C=C double bond.

XPS analysis

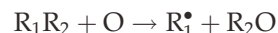
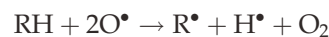
To detect the variation of chemical composition of the GTR surface after plasma treatment, XPS analysis was further conducted. Table I summarizes evidently that the carbon content decreases after atmospheric plasma treatment. However, the oxygen content increases and the ratio of oxygen content to carbon content rose to 15.8%. Figure 3 shows the XPS spectrum of unmodified GTR powder and plasma-treated GTR powder. It is obvious that two new peaks (C1 and C2) with binding energies appeared after the atmospheric plasma treatment, which can be assigned to the C–O species. It indicates that the new oxygen-containing polar groups generated on the GTR powder surface. Because of the bombardment of plasmas species, parts of

TABLE I
Element Content of the Rubber Powder Before and After Plasma Treatment

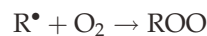
Element name	Untreated rubber powder	Plasma-treated rubber powder
C (%)	87.66	85.3
O (%)	11	13.47
O/C (%)	12.54	15.8

groups were bombarded to generate the free radicals which could be reacted with oxygen directly.¹¹

Reacted with atomic oxygen



Reacted with molecular oxygen



Rubber powder can be brought in lots of oxygen-containing groups, such as carboxyl, carbonyl, and hydroxyl, under the atmosphere of oxygen plasma. Thus rubber powder hydrophilicity is enhanced.

Mechanical properties

The mechanical properties of conventional cement paste, tested under uniaxial stress, cannot correctly reflect the downhole mechanical properties of cement paste. Therefore, the triaxial stress test

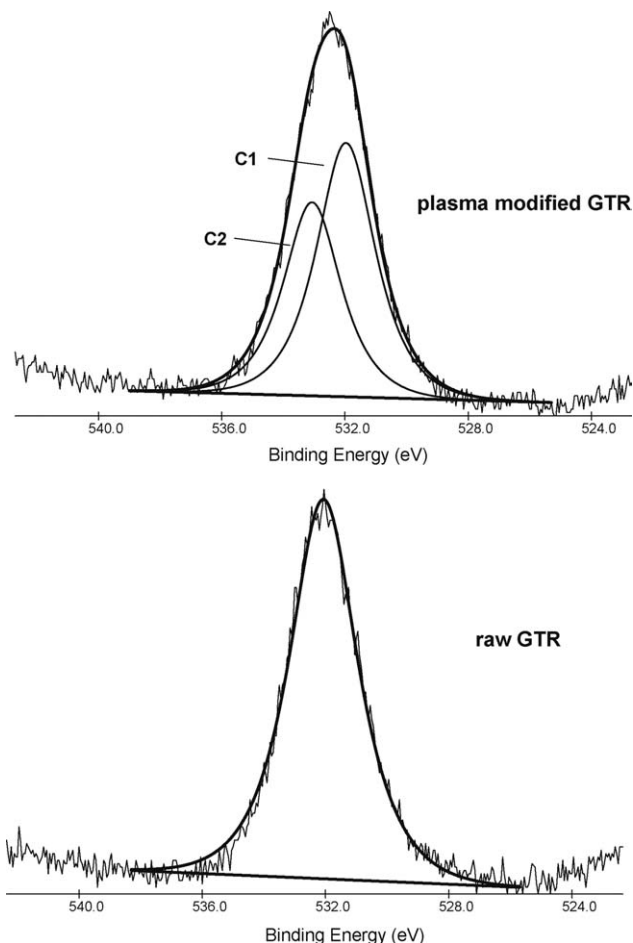


Figure 3 XPS spectrum of raw rubber powder and plasma-treated GTR powder, respectively.

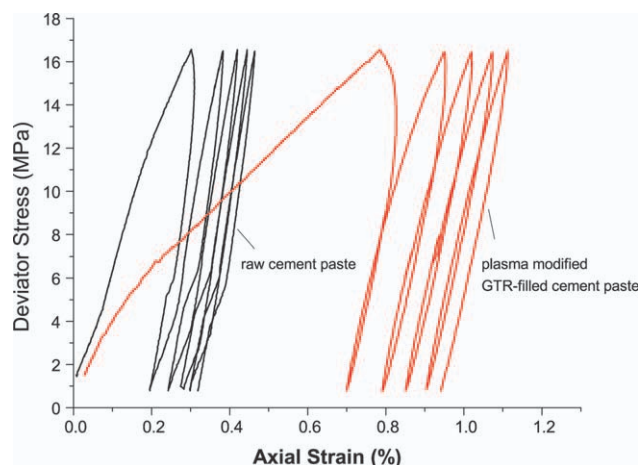


Figure 4 Triaxial stress curve of raw cement paste and plasma-modified GTR-filled cement paste. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigates the influences of rubber powder on cement paste mechanical ability. Figure 4 obviously shows that the plasma GTR-filled cement paste has a more apparent plastic deformation than the raw cement paste in the first cycle period. After that, either raw cement paste or plasma GTR-filled cement paste has a denser stress–strain curve, and both of them have reduced plastic deformation ability. The cycle compaction process of multiperiod stress exists in the two different samples. It reveals the compacting process of pore structure from cement paste to some extent.

The maximum strain of cement paste during the process of stress amplitude is attributed to the plastic deformation ability of porous structural cement paste. Rubber powder added in cement paste makes the ability of plastic deformation higher than raw cement paste. Moreover, with the compaction of

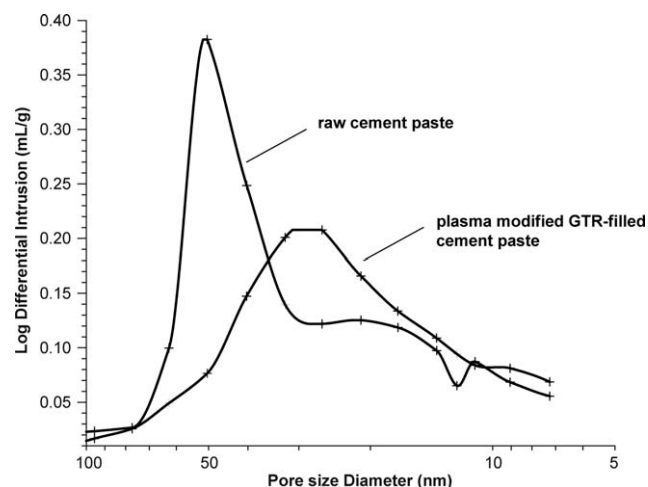


Figure 5 Pore size distribution curve of raw cement paste and plasma GTR-filled cement paste.

multiperiod cycle loading, the elastic deformation ability of rubber powder has been underlined, and the plasma GTR-filled cement paste has higher elastic deformation ability than the raw one in the later loading stage. After GTR powder is added, the plastic deformation and elastic deformation ability of cement paste is enhanced.

Testing of pore size distribution

Figure 5 shows the comparison of pore size distribution curves. It is obvious that the pore size of raw cement paste mainly is distributed in 30–80 nm and the peak values appeared in 50 nm. However, the peak values of plasma-modified GTR-filled cement paste are shifted to the small pore diameter portion, which is close to 30 nm. The cumulative intrusion curve in Figure 6 shows that the percentage of pore size <50 nm in raw cement paste was 60%. However, this percentage rises to 78% in plasma-modified GTR-filled cement. From the variations, it infers that the impermeability of cement paste is enhanced owing to the filling of GTR particles in big pores and the increased compactness of cement paste.

Morphological studies

Figure 7 shows several SEM images of the cement paste, unmodified GTR-filled cement paste, and plasma-modified GTR-filled cement paste. As shown in the SEM micrographs, pure cement specimen in Figure 7(a) has the smooth fracture without evident pores. In contrast, the fracture of unmodified GTR-filled cement specimen in Figure 7(b) is rough and porosity. These pores were caused by extracting rubber particles. It proves that the weak cohesiveness of the interfacial of unmodified GTR particle and

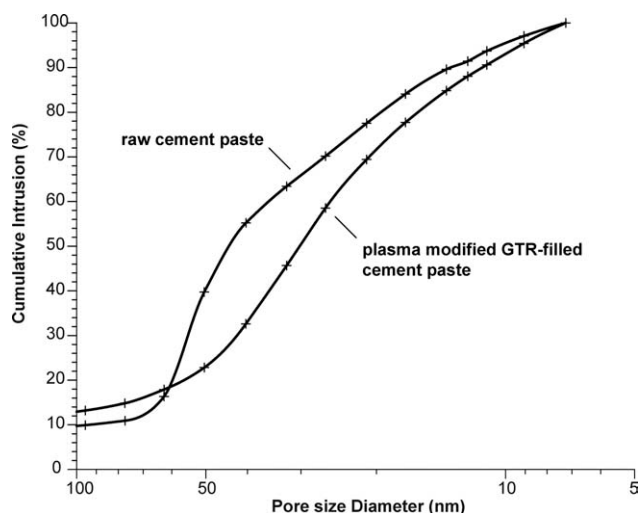


Figure 6 Cumulative intrusion curve of raw cement paste and plasma GTR-filled cement paste.

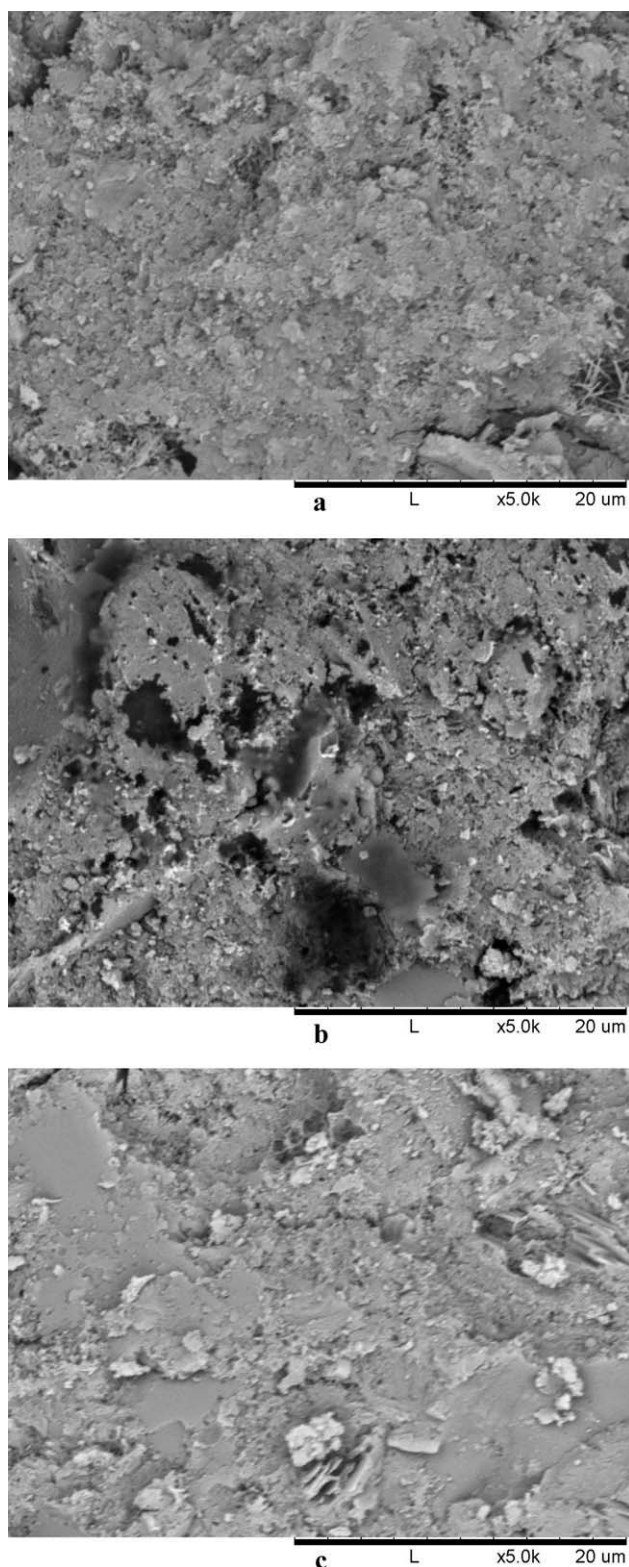


Figure 7 (a) SEM of pure cement paste, (b) SEM of unmodified GTR-filled cement paste, and (c) SEM of plasma-modified GTR-filled cement paste.

cement matrix lead to the decrease of flexural strength. The fracture of plasma-modified GTR-filled cement specimen in Figure 7(c) is as smooth as the

pure cement specimen. It suggests that the plasma treatment is conducive to interfacial adhesion. Meanwhile, some folds, found on the fractured surface, may be formed under loads. When loaded on the specimen, rubber particles absorb some stress, and change the direction of fractures. Besides, owing to the filling of rubber particles in cement matrix pore, the mechanical properties were improved evidently.

CONCLUSIONS

The test investigates the influences of plasma treatment on rubber powder properties and plasma-modified GTR on cement paste. According to ATR-FTIR spectrum, the intensity increase of four peaks at the range of 1400–1600 cm^{-1} indicates that carbon-carbon double bond ($\text{C}=\text{C}$) is generated after plasma treatment. The existence of carbon-oxygen bond ($\text{C}=\text{O}$) after plasma treatment, greatly improving the hydrophilicity of rubber powder, has been confirmed through XPS analysis. The improved plastic deformation and elastic deformation of plasma-modified GTR-filled cement paste are obtained. That is attributed to interfacial bonding between the plasma-modified GTR and the cement matrix. Based on the testing of pore size distribution, the addition of plasma GTR improves the compactness and impermeability of cement paste. Moreover, the SEM micrographs demonstrate that unmodified GTR powder and cement matrix were loosely coupled. Large amount of pores were observed on the fractured surface. In comparison, the fracture of plasma-modified GTR-filled cement specimen is smooth. It indicates that the interface adhesion of plasma-modified GTR powder and cement matrix improves greatly.

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