SURFACE MODIFICATION OF CRUMB RUBBER AND ITS INFLUENCE ON THE MECHANICAL PROPERTIES OF RUBBER-CEMENT CONCRETE

KHUSHBU TAK, UTTAM PANCHORI
ASSISTANT PROFESSOR, ASSISTANT PROFESSOR
DEPARTMENT OF CIVIL ENGINEERING
RAJASTHAN INSTITUTE OF ENGINEERING & TECHNOLOGY, JAIPUR,INDIA

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 hydrophobic nature of rubber, with water contact angle of the rubber surface still higher than 90L [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 LC 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 LC 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 exam-ined by contact angle between water and the surface of rubber with a HARKE-SPCA, Video Optical Contact angle Measurement (Hake Test Instrument, Beijing). The con-tact 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 evalu-ate 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 sat-urated 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 LC 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 ¼ mg=A ð1Þ

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

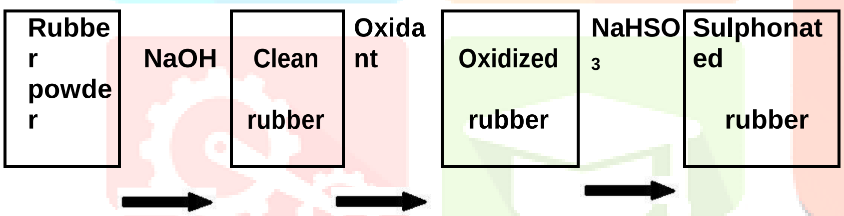

Fig. 1. Flowchart of the rubber modification process.

Fig. 2. Schematic arrangement of the rubber blocks on brick surface

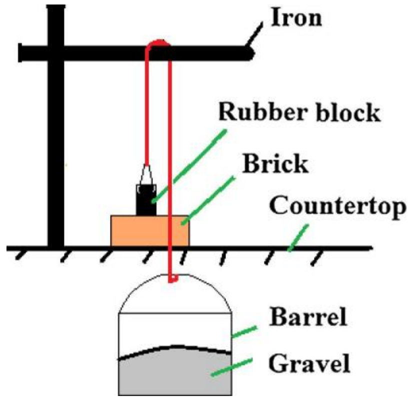

Fig. 3. Self-made adhesive strength test devie

weight 4.5 kg, a bottom diameter 50 mm, and a drop height 457 mm. In the impact test, the hammer of the compactor was always kept in the same height and hit on the same position of the specimen until the first crack appeared. The number of the impact was recorded. The impact energy can be calculated according to formula (2) to characterize the impact properties of materials.

W ¼ Nmgh ð2Þ

where W is the impact energy (J), N is the number of the impact until specimen fail-ure, m is the weight of the hammer (kg); h is the drop height of the hammer (m); g is the gravitational acceleration (9.8 N/kg).

3. Results and discussion

3.1. Oxidant selection

The modified rubber is mainly used in cement matrix material. So, the chlorinated oxidants cannot be used due to the restrictions on chloride ion. Acidic potassium permanganate was chosen as the oxidant to provide a sufficient oxidation condition. After the com-pletion of the oxidation reaction, the excess acidic potassium permanganate can be removed by being rinsed with clear water.

3.2. Effect of sulphonated reaction on the polarity of rubber surface

The purpose of the sulphonated reaction is to increase the surface polarity or hydrophilicity of the rubber, which can be evalu-ated through the change of the contact angle between the rubber surface and the water.

Fig. 4 shows the images of the contact angle testing before and after modification of rubber. It is clear in Fig. 4 that the contact angle of rubber with water is greatly reduced after oxidized-sulphonation. The surface properties of rubber suffered a funda-mental change, from strongly hydrophobic to hydrophilic.

Fig. 5 shows that the contact angle of rubber with water decreases slightly after oxidation, and drops greatly after sulphonation. The water contact angles of original rubber, oxidized rubber, sulphonated rubber (1 h) are 95L, 90.5L, and 71L, respec-tively. The contact angle of rubber with water didn’t change signif-icantly with the increase of the reaction time. It means that the sulphonation reaction almost reached equilibrium after sulphona-tion of 0.5 h. Therefore, a sulphonation reaction of 0.5–1 h is enough for a sufficient sulphonation.

3.3. Infrared spectrum analysis of crumb rubber

The FT-IR spectra of the original crumb rubber and modified crumb rubber are shown in Fig. 6. It shows that multiple bands appear at 1650 _ 1450 cm^{-1} for the original crumb rubber, indicating the existence of C@C or benzene ring. Two strong bands appear at 800 _ 900 cm^{-1} represent C–H bond stretching connecting to carbon-carbon double bond. In the FT-IR spectra of the modified crumb rubber, there are some new bands appeared. Obvious bands appear near 3430 cm^{-1} and 1730 cm^{-1} for the O–H and C@O stretching vibration that are associated with the rubber surface

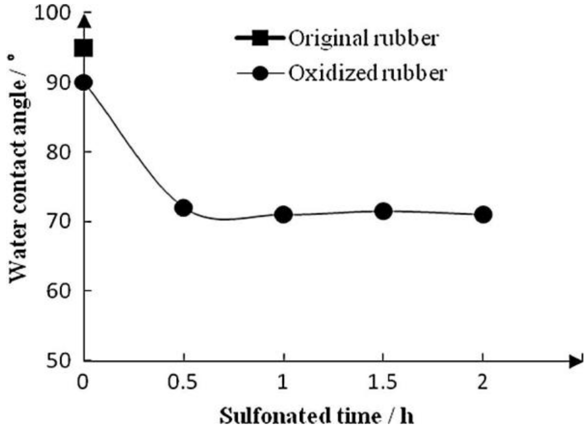

Fig. 5. Effect of sulphonated reaction on the contact angle of rubber surface with wate

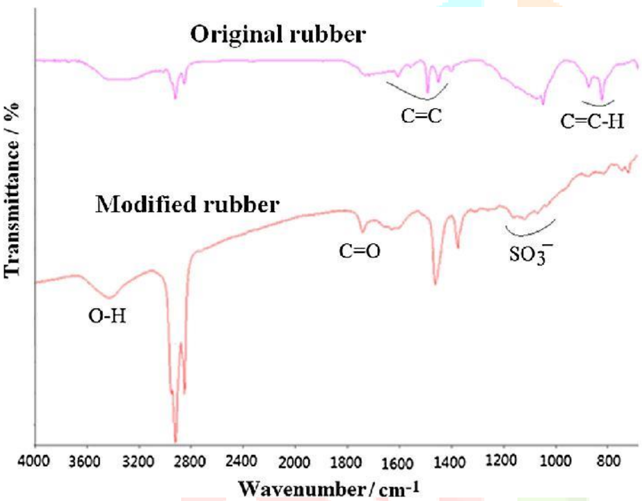

Fig. 6. FT-IR spectra of crumb rubber before and after modification.

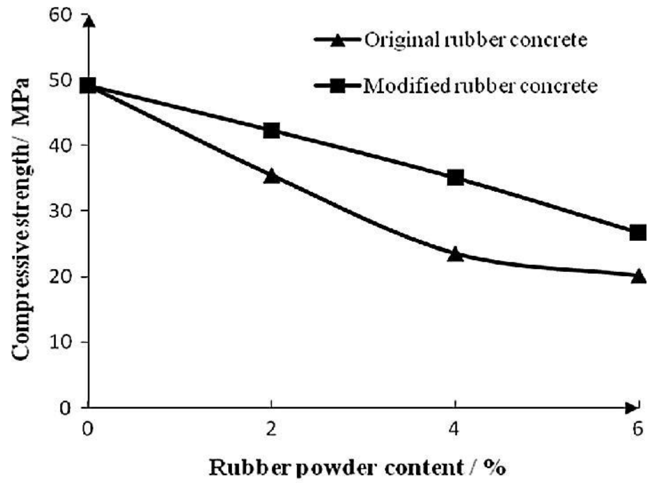

Fig. 8. Relation between rubber content and compressive strength.

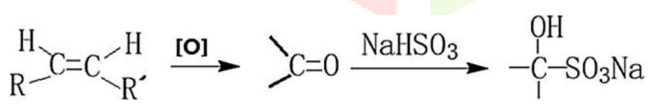

Fig. 7. Reactions during the rubber surface modification.

oxidation. A few weak bands at 1170 cm^{-1}, 1150 cm^{-1}, 1130 cm^{-1}, 1080 cm^{-1} is due to the appearance of SO^-_3 group. The appearances of functional groups are corresponding change of the modification reactions (in Fig. 7) of the crumb rubber.

The oxidation and sulphonation introduced polar carbonyl, hydroxyl and sulfonate groups on the surface of rubber, which made a large number of hydrogen bond and ionic bond between rubber and cement matrix, greatly improving the adhesive strength of rubber and cement matrix and the mechanical proper-ties of the rubber-cement matrix composites. The benefit of the surface modification on the mechanical properties of rubber-concrete will be examined in the following mechanical tests.

3.4. Effect of surface modification on adhesive strength between rubber and cement paste

The adhesive strength between the tire rubber and cement paste before and after modification are shown in Table 1. When removing the maximum and the minimum values (underlined) for each group, the remaining three values were used to calculate the average adhesive strength of the samples.

The adhesive strength between crumb rubber and cement paste is improved by 5.1%, 17.9%, 41.1% respectively due to NaOH treatment, then oxidation, and then sulphonation modification. The oxidation and sulphonation of crumb rubber greatly improves the interfacial bonding property between rubber and cement paste.

Table 1

Adhesive strength between rubber and cement paste/MPa (28 days).

Specimen No.	1	2	3	4	5	Average/MPa
Original	0.218	0.158	0.146	0.204	0.147	0.170
NaOH treated	0.108	0.190	0.212	0.174	0.171	0.178
Oxidized	0.233	0.178	0.194	0.206	0.199	0.200
Sulphonated	0.246	0.238	0.233	0.187	0.279	0.239

AAA3.5. Effect of surface modification on compressive strength of rubber-cement concrete

Since rubber is an elastomer, the incorporation of crumb rubber into cement concrete will greatly reduce the compressive strength of concrete. To maintain a sufficient compressive strength of the concrete, crumb rubber content should be controlled. So, small amounts of crumb rubber were incorporated into concrete to examine the effect on the compressive strength of modified rubber concrete.

Fig. 8 shows the relationship between the compressive strength of the rubber concrete and the rubber content. It can be seen that the compressive strength of rubberized concrete declined rapidly with the increase of the crumb rubber content, and the compressive strength of modified rubber concrete decreased slower. The compressive strength of the concrete with 4% ordinary crumb rubber content reduced to 23.6 MPa from 49.2 MPa, losing 52% of its compressive strength. However, the compressive strength of the concrete was 35.1 MPa when 4% modified crumb rubber was added to the concrete, improving the compressive strength of

Table 2

Concrete impact test results.

Rubber powder content/%	Impact number/times	Impact energy/J
0	3	65.6
4(Unmodified)	5	102.5
4(Modified)	6	124.8

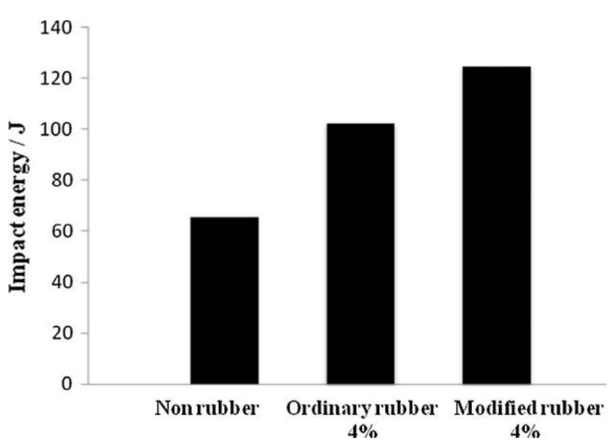

Fig. 9. The impact strength of different concretes.

Fig. 10. Failure modes of concrete specimen subjected to ultimate impact.

concrete with ordinary rubber by 48.7%. This proves that the sur-face modification of crumb rubber can retard the adverse effect of incorporation of crumb rubber on the compressive strength of concrete.

3.6. Impact resistance of cement concrete

The impact resistance of cement concrete is of great significance to its durability and safety. This study simulated the drop-weight test of resistance impact in ACI 544.2 R. to evaluate the impact resistance of concrete. A hammer is dropped repeatedly, and the number of blows required to cause the first visible crack in the test specimen is recorded. This number can be used to estimate of the energy absorbed. The results are shown in Table 2.

Fig. 9 shows the impact energy until the appearance of the first visible crack of the ordinary concrete and concrete with unmodi-fied and modified crumb rubber. It is clear in Fig. 9 that the incor-poration of rubber can effectively improve the impact resistance of concrete. The impact resistance of concrete with modified crumb rubber is 1.9 times of that of ordinary cement concrete. Compared with the concrete with unmodified rubber, the impact energy of modified rubber concrete is also improved by 22%.

Rubber concrete not only can resist greater impact energy, but also shows different failure modes. Fig. 10 shows the failure modes of the concrete after impact strength test. The ordinary concrete suffered a great crushing degree under external impact. The con-crete was brittle and the concrete structure was completely destroyed. The toughness of the concrete is obviously improved by adding crumb rubber, because more intense external impact only produced much narrower cracks. The reason for the improve-ment of the impact strength in the rubber concrete is that the elas-tic rubber particles can disperse local stress. The modified crumb rubber has stronger interfacial chemistry reaction with cement and better stress dispersion effect, resulting in less and narrower cracks and higher impact toughness of the concrete.

4. Conclusions

The surface of the rubber was modified with oxidation and sulphonation and the effect of this modification on the surface property of rubber was examined with contact angle test and FI-IT analysis. The effects of the surface modification of the rubber on the mechanical properties of rubber concrete were studied as well. Based on the results of the study, the following conclusions can be drawn:

1. The surface modification of crumb rubber by oxidation and sulphonation introduced a large number of hydroxyl, car-bonyl and sulfonate groups on the rubber surface. This sur- face modification greatly reduced the contact angel of the rubber with water and the rubber surface turned to be hydrophilic, which can improve the interface reaction between crumb rubber and cement matrix materials.
2.The adhesive property of the rubber and cement paste is improved obviously after the rubber surface modification.

(2) The surface modification method of the rubber proposed in this research is cheap, simple and very effective to enhance the compressive strength and impact strength of rubber-cement concrete.

Acknowledgments

This work was supported by National & Local Joint Engineering Laboratory for transportation and civil engineering materials, Chongqing Jiaotong University (No. LHSYS-2015-04, LHSYS-2014-010).

References

[1] Xiang Shu, Baoshan Huang, Recycling of waste tire rubber in asphalt and portland cement concrete: an overview, Constr. Build. Mater. 67 (Part B) (2014) 217–224.

[2] Jing Lv, Tianhua Zhou, Du Qiang, et al., Effects of rubber particles on mechanical properties of lightweight aggregate concrete, Constr. Build. Mater. 91 (2015) 145–149.

[3] Ali A. Aliabdo, Abd Elmoaty M. Abd Elmoaty, Utilization of waste rubber in non-structural applications, Constr. Build. Mater. 91 (2015) 195–207.

[4] Trilok Gupta, Ravi K. Sharma, Sandeep Chaudhary, Impact strength of concrete containing waste rubber fiber and silica fume, Int. J. Impact Eng. 83 (2015) 76– 87.

[5] Iman Mohammadi, Hadi Khabbaz, Kirk Vessalas, Enhancing mechanical performance of rubberised concrete pavements with sodium hydroxide treatment, Mater. Struct. 49 (3) (2016) 813–827.

[6] Nadia Segre, Paulo J.M. Monteiro, Garrison Sposito, Surface characterization of recycled tire rubber to be used in cement paste matrix, J. Colloid Interf. Sci. 248 (2) (2002) 521–523.

[7] Haibo Zhang, Mifeng Gou, Xiaoxing Liu, et al., Effect of rubber particle modification on properties of rubberized concrete, J. Wuhan Univ. Technol. Mater. 29 (4) (2014) 763–768.

[8] Obinna Onuaguluchi, Effects of surface pre-coating and silica fume on crumb rubber-cement matrix interface and cement mortar properties, J. Clean. Prod. 104 (2015) 339–345.

[9] L.P. Rivas-Vázquez, R. Suárez-Orduña, J. Hernández-Torres, et al., Effect of the surface treatment of recycled rubber on the mechanical strength of composite concrete/rubber, Mater. Struct. 48 (9) (2015) 2809–2814.

[10] Trilok Gupta, Sandeep Chaudhary, Ravi K. Sharma, Mechanical and durability properties of waste rubber fiber concrete with and without silica fume, J. Clean. Prod. 112 (Part 1) (2016) 702–711.

[11] Gregorio Ossola, Adam Wojcik, UV modification of tire rubber for use in cementitious composites, Cement Concr. Comp. 52 (2014) 34–41.

[12] Qiao Dong, Baoshan Huang, Xiang Shu, Rubber modified concrete improved by chemically active coating and silane coupling agent, Constr. Build. Mater. 48 (2013) 116–123.

[13] Changhui Yang, Baoquan Liu, Yanan Zheng, Effects of modification of recycled tire rubber particles on strength of crumb rubber concrete, Mater. Rev. China 27 (12) (2013) 113–116.