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Study on surface modified basalt fiber reinforced unsaturated polyester resin with silica-carbon black

G Y Gong, J C Liang and K F Yu¹

Department of Materials Science and Engineering, Jilin university, China.

¹ E-mail: yukf@jlu.edu.cn

Abstract. In view of the strong chemical inertia and poor wettability of basalt fiber, its surface was treated by modified silica-carbon black particles. The surface roughness of basalt fiber was observed by scanning electron microscope (SEM). The change of fiber contact angle was measured. And the mechanical properties of fiber composites plate were tested. After the treatment, the results showed that the surface roughness of basalt fiber was increased and the wettability of the fiber was improved. The flexural properties and impact resistance of fiber reinforced unsaturated polyester resin were improved greatly. Compared with KH-570, the effect of KH-550 modified particles on basalt fiber was better than that of KH-570. Therefore, silica-carbon black as a modified particle to treat basalt fiber was a feasible solution.

1. Introduction

Unsaturated polyester resin (UPR) is one of the most widely used thermosetting resins. Because of its light weight, corrosion resistance, simple production process and low maintenance cost [1]. Due to the low strength and poor hardness of unsaturated polyester resin, it is usually necessary to modify for the better comprehensive properties of unsaturated polyester resin composite. Using fiber to strengthen resin is an effective way to improve the performance of resin. Among numerous composite materials, glass fiber reinforced composite is one of the most used composites. It has the advantages of high strength, high temperature resistance, corrosion resistance and so on [2]. However, the glass fiber reinforced composites have some problems, such as the difficulty of waste recovery and environmental pollution [3].

Basalt fiber is a kind of continuous fiber material, which uses natural basalt as raw material made by melting at high temperature and through a platinum-rhodium alloy drawing leaky plate [4,5,6]. It not only has good mechanical properties, but also has high temperature resistance, corrosion resistance, chemical stability, electrical insulation, moisture absorption, etc [7]. Basalt fiber is mostly used as the reinforced phase of composite materials [8]. It has a wide range of applications in the field of aerospace, automotive lightweight, building, chemical and medical equipment. Basalt fiber, carbon fiber, aramid fiber and ultra-molecular weight polyethylene fiber are listed as the four kinds of vital fiber needed to develop in China.

The strength of basalt fiber is between glass fiber and carbon fiber. In a certain extent, basalt fiber also can be used as a substitute for carbon fiber and glass fiber because of its balance between properties and cost-effective [9]. At the same time, the production process of basalt fiber is more environmentally friendly. It is also a kind of green inorganic fiber material with low raw material cost and the less energy consumption [10]. Due to the melting and drawing process of basalt, the fiber section is circular and the fiber surface is very smooth under the effect of surface tension [11]. When it



is used in the preparation of fiber composites, the combine between the smooth fiber surface and the matrix material are poor [12]. It is hard for fiber to bond with the substrate closely. Fiber reinforced composites bear and transfer loads through the interaction of fiber, resin and interface [13]. The performance of the interface has a great effect on the performance of fiber-reinforced composites [14]. If the bond between basalt fiber and resin matrix materials is carried out not well, it will bring more gaps and imperfections. If the interface is not complete, it will lead to stress concentration and the weak of the ability of the interface layers to transfer load [15]. To improve the interfacial properties of composites, it is necessary to take some modifications on fiber surface.

In view of the similarity between basalt fiber and glass fiber, the methods of surface treatment on basalt fiber used by domestic and foreign researchers are referenced from glass fiber surface treatment. There are mainly coupling agent treatment [16], surface coating modification [17], plasma surface modification [18], acid and alkali etching methods [19,20] and other types.

Silica-carbon black is a two-phase material. Bio-carbon and silica are two kinds of material with different physical and chemical properties. Biochar usually has rich surface functional groups (C=O, C=O, -COOH, -OH, etc) [21], which is benefit for resin to bond. The rice husk is treated through selective pyrolysis, directional crushing to produce mixing homogeneous silica-carbon two-phase materials. Silica was coated by bio-carbon, which shielded the hydroxyl group, then hindered the agglomeration effect of silica ball, so silica-carbon black materials have good dispersibility. The size of silica-carbon black particles is among 1-8 μm . After the nitrogen protection ball mill treatment, particle size is reduced to hundreds of nano level. It can meet the size requirements of fiber surface modification.

In this paper, silica-carbon black was used as modified particle, it was processed by ball milling, then the particle was modified by silane coupling agent. Treated silica-carbon black particle was grafted on basalt fiber by silane coupling agent. The flow adhesion of suspension solution was adhered, the micro-flow could resist the agglomeration sedimentation effect, and the steps of emulsion method were omitted. After treated, the silica-carbon black was grafted on the fiber, and the basalt fiber was modified. The surface roughness of basalt fiber was increased. The infiltration was improved. And the flexural and impact properties of composites were increased greatly.

2. Experiment part

2.1. Experiment materials and equipment

2.1.1. Materials. Basalt fiber unidirectional fabric: Jiangsu Tianlong Basalt Fiber Co., Ltd, China; Unsaturated polyester resin 196: Jiangsu Fullmark Chemicals Co., Ltd, China; Cobalt naphthenate: Shanghai three chemicals fine chemical plant, China; Methyl ethyl ketone peroxide: Butanox M-50, Tianjin AkzoNobel Peroxide Co., Ltd, China; Tri-butyl phosphate: Tianjin DingFu Chemical factory, China; Silane coupling agent: KH-550, KH-570, Nanjing Chengong, China; Silica-carbon black (homemade); Glacial acetic acid: A.R. Beijing Chemical Works, China.

2.1.2. Equipment. Planetary ball mill: XQM-2, Changsha Tencan Powder Technology Co., Ltd, China; Hydraulic press: XLB50 \times 2 Zhengzhou Zhong yang Mechanical Equipment Co., Ltd, China; Heat-collecting agitator: DF-101s, Jiangsu analytical instrument, China; Electric blast drying box: 101A-1ET, Shanghai experimental Instrument factory, China; Universal testing machine: WSM-5KN, Changchun Institute of Intelligent Testing machine China; Memory Impact Tester: JJ-20, Changchun Intelligent Instrument Equipment Co., Ltd, China; Scanning electron microscope: JSM-6700F, JEOL, Japan.

2.2. Experiment procedure

2.2.1. Silica-carbon black treatment. Silica-carbon black was placed in planetary ball mill with nitrogen protection, then treated with ball mill for 8 hours. The silica-carbon black particles were refined to reach the nano meter level. It met the requirements of fiber adhesion. First, 1 g refined silica-carbon black was dispersed in 200 mL deionized water, stirred on the magnetic stirrer for 2 hours to prepare the suspension solution. Then the large particle precipitation was removed from the suspensions. And kept suspensions in a micro-stirring environment.

2.2.2. Fiber fabric treatment. First, we cut the basalt fiber fabric to the size of 250 mm length and 200 mm width, rinsed the dust off the fiber surface with water. Then we placed it in a drying box at 60 °C. 2 mL silane coupling agent KH-550 was put in 200 mL Hydrolysis of deionized water and added 5 mL glacial acetic acid to keep coupling agent solution in an acidic environment. Put the solution on magnetic stirrer under the condition of stirring at 60 °C water bathing for 2 hours to accelerate the hydrolysis of silane coupling agent, until the solution was transparent and without precipitate. The suspensions were poured into the prepared silane coupling agent solution, and the stir was continued under the water bath condition for 2 hours, allowed the coupling agent solution to fully react with silica-carbon black.

The suspensions were easy to precipitate under the condition of static, so it was necessary to exert some stirring force to resist precipitation. The basalt fiber fabric was rolled into a roll in a homemade suspended container to ensure that every surface of the fabric was fully contacted with the suspensions. In the magnetic stirring environment, the suspensions were in a flowing state, and the suspension particles had fully reacted with the fiber for 2 hours to complete the attachment process. The modified basalt fiber fabric was treated with ultrasonic cleaning to wash away the residual silica-carbon black particles which not participate the graft reaction. Then the treated basalt fiber fabric was put in drying box to dry and prepared for use.

Repeat the above experiment. Silane coupling agent KH-570 was used to treat silica-carbon black particles instead of KH-550. Remaining steps of above experiments remained unchanged. We got another treated basalt fiber fabric, prepared for use.

2.2.3. Preparation of fiber-reinforced polymers. First, we put 180 mL unsaturated polyester resin (196) into the beaker. Ensuing 2 mL naphthenic acid cobalt was fully stirred in unsaturated polyester resin. Then 0.4 mL tri-butyl phosphate was dropped into the unsaturated polyester resin to eliminate the bubble. Finally, 2 mL methyl ethyl ketone peroxide was added into resin under evenly stirring. The basalt fiber fabric was paved in the PTFE mould, the fiber fabric had three layers, poured the resin into mould, put the mould on the hydraulic press. Composite materials were cured for 30 minutes under 50 °C heating conditions. The fiber volume content of the pouring composite plates was about 13%. After repeating the above experiment, the untreated fiber reinforced composite plates and the modified fiber reinforced composite plates were prepared. The fiber composite plates were treated into standard specimen by mechanical processing, and the mechanical properties of the composite plates would be tested in the following steps.

2.3. Test and characterization

Impact performance Test: According to GB/T2567-2008, we prepared the type II no notch small sample, the specification was 80 mm × 10 mm × 4 mm, the span of L was 60 mm; At least 6 groups of same specimens were prepared with one composite plate. And the impact properties of the materials would be tested by impact tester.

Three-point bending performance test: According to GB/T2567-2008 to prepare bending specimens, sample specifications for 80 mm × 15 mm × 4 mm. At least 6 groups of same samples were prepared with one composite plate. The bending properties of the materials would be tested by universal tester.

The surface morphology of basalt fiber before and after modified treatment was carried out by scanning electron microscope (SEM). The effect of fiber modifications was judged by the change of the surface morphology of the fiber before and after modifications. And the section of the composites was analyzed to reflect the condition of the combination of fiber and resin.

Contact angle was an important index to measure the ability of liquid to solid infiltration, and the wetting degree of liquid to solids could be indicated by contact angle. A shape analyzer was used to observe the shape of the droplet of the infiltrating fiber. Because the water droplets were too small, the instrument could not directly measure the contact angle between the fiber and the water droplet. According to the definition of contact angle, we took the point at the intersection of the solid-liquid gas three points, took the intersection point as the tangent of the solid and liquid, liquid and the gas, and measured the angle of the two tangent lines to get contact angle.

3. Results and discussions

3.1. Morphology of basalt fiber

The basalt fibers before and after modifications were analyzed by SEM[22]. Figure 1 (a) showed the untreated basalt fiber with smooth surface. When the basalt fiber was used in composites, the interface of composites would be damaged easily under the effect of external forces. Figure 1 (b) presented the morphology of the basalt fiber which had been treated by the modified silica-carbon black with KH-550. The modified silica-carbon black particles were successfully attached to the surface of the basalt fiber. We could see particles of different sizes on the surface of fiber. Compared with the untreated basalt fiber, the surface roughness of the basalt fiber was improved obviously. The rough surface could provide more areas for the unsaturated polyester resin to bond, when the fiber was used in composites.

Figure 1(c) described the basalt fiber which had been treated by modified silica-carbon black particles with KH-570. In the same way, there were also many particles adhering to the basalt fiber, and the surface of fiber became rougher than before. But particle density was lower than that in Figure 1(b).

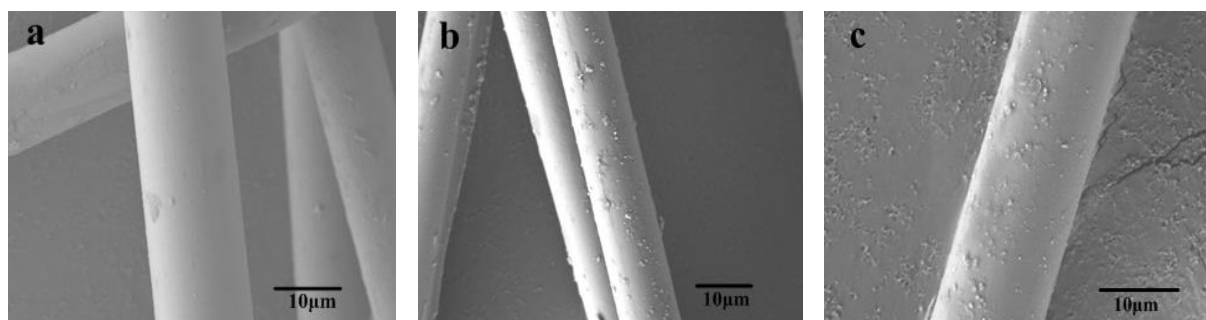


Figure 1. Morphology of basalt fiber (a) untreated basalt fiber; (b) basalt fiber after being modified with silica-carbon black (treated by KH-550); (c) basalt fiber after being modified with silica-carbon black (treated by KH-570).

3.2. Mechanical properties

The test results of the impact strength of the composites were exhibited in Figure 2. When the modified silica-carbon black was used to treat basalt fiber, the mechanical properties of the composites were improved greatly. Compared with the untreated fiber composites, the impact performance of the basalt fiber composites treated by silica-carbon black (KH-550) was increased from 66.5 kJ/m² to 80.0 kJ/m². The increase rate was 20.3%. When the KH-570 was used to treat fiber, impact performance of composites was increased from 66.5 kJ/m² to 72.9 kJ/m². The increase rate was 9.6%.

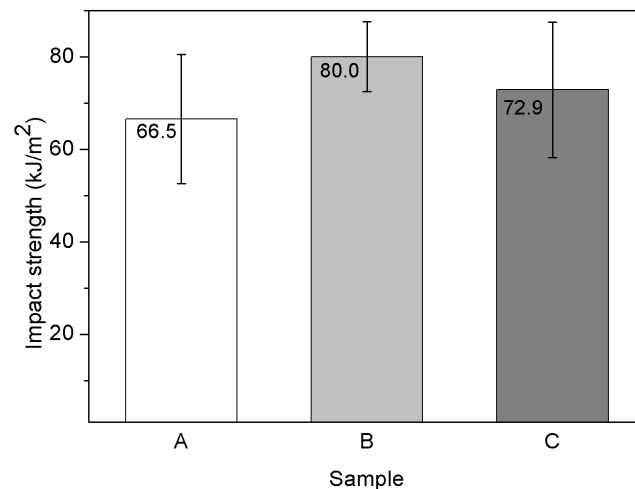


Figure 2. Impact strength of composites (A: untreated basalt fiber; B: fiber modified by silica-carbon black (KH-550); C: fiber modified by silica-carbon black (KH-570)).

As shown in Figure 3, the bending strength of untreated basalt fiber composites was 65.2 MPa. After modified by silica-carbon black (KH-550), it was increased significantly from 65.2 MPa to 105.1 MPa. The bending performance of that treated by KH-570 was increased from 65.2 MPa to 88.0 MPa.

It was obvious to be seen that modified silica-carbon black had some influence on the mechanical properties of basalt fiber reinforced composites, and the mechanical properties increased greatly when basalt fiber was treated by silica-carbon black. KH-550 was more effective than KH-570 when it was used to modify silica-carbon black.

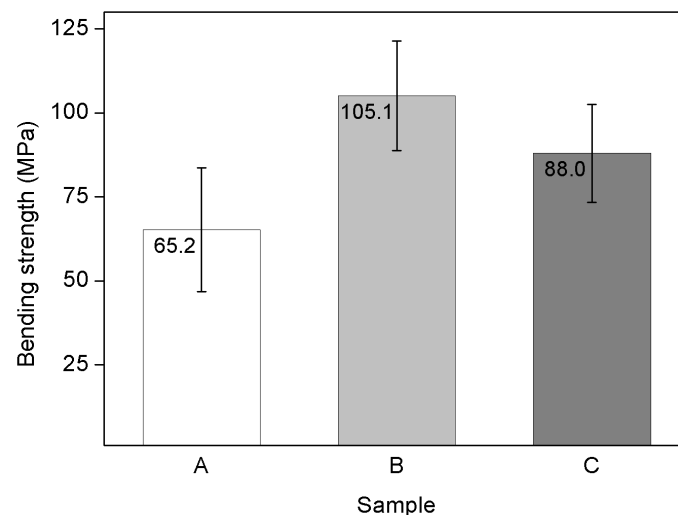


Figure 3. Bending strength of composites (A: untreated basalt fiber B: modified by silica-carbon black (KH-550); C: modified by silica-carbon black (KH-570)).

3.3. Section analysis of composites

The impact section of the composites was scanned by SEM, and the results of the scanning were shown in the following Figure 4. When the untreated fiber was used to enhance unsaturated polyester resin, the material section was tidier after receiving the shock, and the fiber pull-out fracture was more

obvious. As shown in Figure 4 (a), the resin matrix fracture position did not coincide with the fiber fracture position, and the fiber had obvious tendency to pull out from the matrix. The results showed that the combine of fiber and composite material was poor, and the fiber may not play a better buffering effect when it was subjected to stress.

As shown in Figure 4 (b), the fiber was treated by silica-carbon black which had been modified by KH-550. When the treated fiber resin composites were under stress, the fracture position of fiber was near the interface of the matrix resin, and the fiber was covered with the resin. There was no obvious pull-out fracture, the fiber had a better cushioning effect on the composites; Figure 4 (c) presented the impact section of basalt fiber composite materials treated by the KH-570 modified silica-carbon black. We could see from the picture (c), when composites were broken, the pull-out fracture of fiber in the material section was not obvious, but the length of exposed fiber was more than that of another group shown in Figure 4 (b). The coating effect of the resin on the fiber was not as better as that shown in Figure 4 (b), and the effect of the modified fiber was much better than that of the untreated basalt fiber.

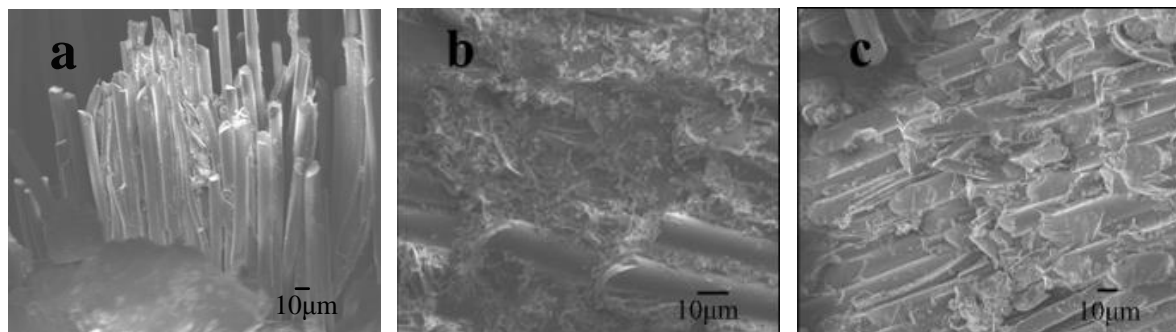


Figure 4. Impact section of composites (a) untreated basalt fiber composites; (b) basalt fiber composites modified by silica-carbon black (KH-550); (c) basalt fiber composites modified by silica-carbon black (KH-570).

3.4. Fiber contact angle test

Figure 5 (a), (b) and (c) were the contrast images of basalt fiber infiltrated by the water droplet. Figure 5 (a) was the untreated basalt fiber, the water droplet was hanged on the fiber, the contact angle of the fiber was $86.0 \pm 4.1^\circ$ and it was close to the right angle. In Figure 5 (b), we could find the difference that the shape of droplet was not as round as that in Figure 5 (a). The water droplet tended to infiltrate on the basalt fiber. The contact angle of fiber and resin was $51.5 \pm 3.9^\circ$. Compared with untreated fiber, its contact angle decreased by 40.1%. The modified silica-carbon black had some effect to improve the infiltration of basalt fiber. The shape of droplet on treated fiber which had been modified by silica-carbon black (KH-570) was also not round. It was similar with that in Figure 5 (b). The contact angle of droplet and fiber was $59.5 \pm 2.3^\circ$, and compared with the untreated fiber, it decreased by 30.8%.

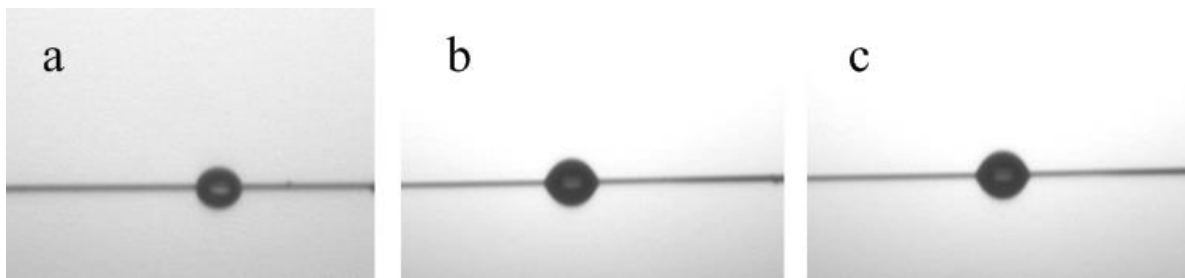


Figure 5. Contact angle of fiber and water (a) untreated basalt fiber; (b) basalt fiber after being modified with silica-carbon black (treated by KH-550); (c) basalt Fiber after being modified with silica-carbon black (treated by KH-570).

In a conclusion, both kinds of silane coupling agent had effects on modifying silica-carbon black. And when the KH-550 was used to modify silica-carbon black, the effect of improving fiber infiltration was slightly better than that used KH-570.

4. Conclusions

(1) After the process of the basalt fiber treated with modified silica-carbon black, the silica-carbon black particles attached to the fiber successfully, and the smooth surfaces of fiber became coarse. It was indicated that the modified silica-carbon black had functions to improve roughness of surface.

(2) By contrasting the mechanical properties of the fiber reinforced unsaturated polyester resin composites, the impact resistance and flexural properties of the composites which was modified by silica-carbon black were greatly improved. The modification effect of silane coupling agent KH-550 on silica-carbon black particles was better than that of KH-570, and the mechanical properties of modified composites were more obvious.

(3) After modified by silica-carbon black particles, the contrast of the raw silk with the original filament became smaller, and the infiltration of fiber became better.

(4) By attaching the fiber fabric with silica-carbon black suspensions in the micro-flow environment, the settlement of the modified particle was solved simply and effectively, and the solution flow could make the adhesion reaction more uniform. Therefore, silica-carbon black suspensions to modify basalt fiber was an effective surface treatment method. The best modification effect of silica-carbon black on basalt fiber still needed to be further explored.

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