Heat resistance of basalt fiber enhanced by silicious-fluoric-PAA hybrid sizing agent

Z T Wang¹, H J Luo*¹, Q L He¹, H Jiang²

¹School of metallurgy, Northeastern University, Shenyang, Liaoning, China
²TIANCHENG Environmental Protection technology co., Ltd, Fushun, Liaoning, China

Abstract. Basalt fiber, as a high strength and good temperature resistance inorganic material, has an excellent application in the high temperature filtration industry, but its strength retention decreases obviously with time going when baked at temperature above 300°C. This limits the range of its application as a filter material. In this paper, the sizing agent was prepared by mixing polytetrafluoroethylene, silane coupling agent, polyacrylate acid, polymeric acid and polyurethane crosslinking agent in aqueous solution together, and then the surface of basalt fiber was coated by the sizing agent. The experiment results showed that the emulsion droplets formed in the aqueous solution had small particle size and good dispersibility. The initial decomposition temperature of the film formed by the sizing agent was 220°C. The initial tensile strength of the coated basalt fiber was 60% higher than that of the uncoated fiber at room temperature. The residual strength of the coated fiber was 6 times higher than that of the uncoated fiber when treated at 340°C for 10 hours.

1. Introduction
Basalt fibers are mineral fibers produced by the melting of volcanic rocks, and then stretched into continuous filaments which are generally have diameters of 7-13 μm [1]. Basalt fiber, as a cost-effective fiber, has the advantages of high strength, high temperature resistance, environmental friendly and degradable, which conform to the development direction of high-temperature filtration materials [2,3]. However, when the treated temperature is above 300°C, the internal structure of basalt fiber changes due to oxidation and crystallization, which leads to brittle and strength decrease, thus limited the range of its application and service life. For example, when basalt fiber is used as a high-temperature flue gas filtration material, the expected temperature is 300-350°C. In this temperature range, the strength of basalt fiber decays rapidly [4], with an attenuation of 40% in 1 hour and 80% in 3 hours. If the problem of strength decaying too fast at this range cannot be solved, the basalt fiber will not be able to be used for a long time under this working condition.

One of the methods to overcome this problem is to coat the fiber surface. This method is simple, facile and effective. Shayed et al. [5] coated basalt fiber with polysiloxane or polysilazane. The results showed that the initial strength increased 70% and the strength retention rate was 65-90% at 500°C. However, this method used ethyl acetate as the solvent, which was high costs. And the coated basalt fiber was inflexible, so it cannot be used for subsequent textile processing. Organic materials such as polyurethane [6], vinyl resin [7], and epoxy resin [8,9], and inorganic materials such as SiO₂ [10] and graphene oxide [11], have been reported as surface modifiers for basalt fibers. However, none of the above reports mentioned the strength variation of basalt fibers at 300-350°C, where was the expected condition of the high-temperature flue gas filtration.
In this paper, a basalt fiber sizing agent was prepared by mixing polytetrafluoroethylene (PTFE), silane coupling agent, polyacrylic acid (PAA), polysilicic acid (PSA) and polyurethane crosslinking agent agent in aqueous solution together. At the same time, the particle size analysis of the sizing agent was carried out. Thermogravimetric (TG) analysis and Fourier transform infrared (FT-IR) analysis of its films were carried out. Tensile tests of the coated fiber at 340℃ with different treated time were carried out and characterized by electron microscope (SEM). The mechanism of basalt fiber reinforcement by sizing agent and mechanism of film forming of the sizing agent were discussed.

2. Experimental

2.1. Material
Basalt fiber was supplied by Shanxi BASALT Technology co., LTD., which produced by combining multiple parallel filaments without twist. The basic parameters of the basalt fiber are listed in Table 1.

| model | Diameter/μm | Leaner density/tex | tolerance/te | Moisture content/% |
|-------|-------------|--------------------|--------------|-------------------|
| CBF7-400 | 7           | 400                | ±20          | <0.2              |

PTFE emulsion Uses DISP 30LX produced by Dupont co., LTD.. PAA and PSA were all made by TIANCHENG Environmental Protection technology co., Ltd in Fushun. The crosslinking agent of diisocyanate is full-sealed polyurethane emulsion. Silane coupling agent is vinyl triethoxy silane (A151), which purchased from www.Macklin.com.

2.2. Configuration of Sizing Agent
The optimum ratio of sizing agent was determined by orthogonal test: w[PTFE]=11%, w[A151]=1.5%, w[PSA]=12%, w[crosslinking agent]=5%. The content of PAA was determined by film-forming test as 5%, and the remaining component was water as the solvent.

2.3. Coating Method
The cut basalt fiber single yarn was keep in an oven at 380℃ for 2 min to desize the commercial sizing agent. The sizing agent was mixed the sequence of PTFE, PAA, PSA, diisocyanate crosslinking agent silane coupling agent and water. The fiber bundles were immersed in the sizing agent and dried in an oven at 160℃ for 2 min. The samples were then cured at 230℃ for 15 min.

2.4. Characterization
Particle size analysis: take 2 mL of the sizing agent, then appropriate amount of deionized water was added as dispersant and stirred. 1 or 2 drops were put into the sample pool, and the Master Sizer 2000 laser particle size analyzer produced by Malvern instruments co., Ltd. was used to determine the particle size and distribution by static non-ultrasonic vibration method under the condition of 10 shading ratio. TG analysis: the sizing agent was stirred and dispersed, then cured at 230℃ for 15 min, and dried at 60℃ for 10 h. TG analysis was performed at STA449F3 produced by NATCH, Germany, in air atmosphere with the heating rate of 20℃/min.

FT-IR analysis: the sizing emulsion was uniformly coated on the glass slide and placed in a vacuum drying oven at 230℃ for 15 min. The prepared film was removed and tested by a Nicolet 6700 fourier infrared transform spectrometer.

Tensile strength analysis: the single yarn were cut into 30 cm, and the tensile strength of the coated fiber was performed at YG028 electronic strength machine manufactured by Changzhou ZHENGDA general textile instrument co., LTD. According to the standard test method ASTM D 3379-75, setting the loading speed at 2 mm/min and conduct tensile test until the single yarn was broken.

SEM observation: the sample were cut into 2mm and glued to the sample table horizontally and vertically with conductive adhesive. The morphology of the sample was observed by the scanning
electron microscope SSX-550 produced by SHIMAZU company Japan. The acceleration voltage was 20 kV. The surface of the sample was sprayed with gold before the test.

3. Results And Discussion

3.1. Particle size analysis

In order to investigate the dispersibility of sizing agent emulsion in water, particle size analysis of PTFE/PAA mixture emulsion, unstirred sizing agent and stirred sizing agent were tested by laser particle size tester, the results are shown in figure 1. It can be seen from the curve of PTFE/PAA emulsion that the particle size distribution is concentrated (with the distribution index of 0.090) and the particle size is small (which concentrated at 120 nm). From the curve of the sizing agent without stirred, the particle size distribution is scattered (with distribution index 0.175) and the particle size is large (which concentrated at 191 nm). In order to reduce the aggregation effect, the sizing agent was magnetic stirred for 15 min, and ultrasonic dispersed for 10 min. It can be seen that the particle size distribution is dramatically improved, which is concentrated at 140 nm, with the distribution index of 0.120. The particle size of the sizing agent emulsion is lower than that of unstirred emulsion but better dispersion, it can attributed that the surface of PSA contains a lot of hydroxyl which ensure the dispersibility in the hybrid solution.

![Figure 1. Particle size distributions of the emulsions](image)

3.2. TG analysis

In order to characterize the thermal stability of the film formed by sizing agent, TG analysis was carried out. figure 2 shows the TG analysis curves of films under air atmosphere, and the heating rate was 20 °C/min. The three curves represent the heat loss of PAA film, PTFE/PAA composite film and sizing agent film. It can be seen from fig. 2 that the three kinds of membranes have similar stages of heat mass loss. The mass loss below 100°C is attributed to water evaporation. The initial thermal decomposition
temperature of PAA is 150℃, and the addition of PTFE increases the decomposition temperature of the system by about 40℃, which indicates that the addition of PTFE is effective to improve the thermal stability of the system. The addition of inorganic silicon further increase the decomposition temperature of the system by about 30℃. The initial decomposition temperature of the system is 220℃, which is 47% higher than that of the PAA system. The reason can be explained by inorganic silicon is connected with PAA by chemical bond through coupling agent, and the bond energy of Si-O and F-C are very high. It can be concluded that the sizing agent system has good temperature resistance.

3.3. FT-IR analysis
In order to characterize the molecular structure of the sizing agent, fourier transform infrared analysis was carried out. Figure 3 is the fourier transform infrared spectrum analysis diagram of sizing agent film. The wide band at 3465 cm\(^{-1}\) is related to -OH vibration, which mainly from PSA. The absorption peaks between 2980 and 2878 cm\(^{-1}\) are related to -CH\(_3\) and -CH\(_2\)- vibration. The peak at 1735 cm\(^{-1}\) is the stretching vibration peak of C=O. The peak at 1453 cm\(^{-1}\) is the characteristic peak of acrylate. The peaks at 1250 cm\(^{-1}\) and 1167 cm are C-F absorption peaks from PTFE. A series of absorption peaks at 1100~1000 cm\(^{-1}\) are strong absorption bands of Si-O-C. The absorption peak at 1066 cm\(^{-1}\) proves the existence of Si-O-C bond, indicating that the PSA formed chemical bonds linking with the organic components of the carbon chain.

![Figure 3. FT-IR spectra of the sizing agent](image)

3.4. Tensile properties of coated fibers
In order to characterize the relationship between the tensile strength of basalt fibers and heating time at high temperature, the tensile strength of coated basalt fibers and uncoated basalt fibers. figure 4 shows the variation of the strength of basalt fiber during heat treatment (340℃) over time, where each point is taken average from the data of 10 samples. Without treatment, the tensile strength of coated fiber (295 N) is 60% higher than that of uncoated fiber (186 N). When heat treatment time is less than 0.5 h, the residual strength of coated fiber is 60% higher than that of uncoated fiber. With the extension of heat treatment time, the residual strength of uncoated fiber declines sharply, which is attributed to the oxidation of ferrous iron in the fiber to ferric iron, leading to the change of internal structure of the fiber, and making the fiber brittle. For the coated fiber, the surface membrane of the fiber isolates oxygen, which effectively slow down this trend, so as to play the important role of fiber reinforcement. After 10 h of heat treatment, the residual strength of the fiber is 91 N, which is 6 times higher than the 15 N of the uncoated fiber, and this strength is enough for industrial application. The residual strength of the coated fiber decreases with the extension of time, which can be attributed to that the high temperature causes the organic components on the surface of the fiber to crack firstly and the membrane structure to loosen gradually. However, inorganic components of the membrane can still protect the fiber in a certain extent and disperse the stress.
3.5. SEM observation

Figure 5 shows the SEM images of coated basalt fibers at 340°C for 0 h, 10 min, 30 min and 6 h. It can be seen that the surface of the fiber is smooth before heat treatment (figure 5(a)). With the extension of treatment time, cracks appeared somewhere on the surface (figure 5(b), 5(c)), which damaged the integrity of the coating, but still can maintain the complete coverage of the fiber surface. The organic components are completely decomposed within 6 h (figure 5(d)). The surface is no longer smooth, and there are obvious defects aggregate into humps somewhere.

In order to more obviously observe the transformation of the coated fiber at high temperature, SEM observation were carried out on its cross-section photos (see figure 6). Through the figure 5, it can be seen that the film on the fiber surface. Before treatment, the fiber surface is compact smooth and link with the film covering. After 10 h heat treatment, the film gradually expanded and loosen, but still covering the surface of the fiber.

Figure 5. SEM images of coated basalt fibers treated at 340°C for 0 h (a), 10 min (b), 30 min(c) and 6 h(d)
3.6. Film forming mechanism

Figure 7 is a schematic diagram of the film formation reaction of the sizing agent. Where the right of the arrow are schemes of PAA and PSA, and the left of the arrow is the scheme of organic-inorganic network. PSA is a kind of spherical inorganic particles. The surface of PSA has active hydroxyl group, which can form stable chemical bonds with carbon chain polymers through coupling agent, and then a stable organic-inorganic hybrid film is formed. Generally, the rigidity, density and heat resistance of the membrane increase with the increase of the content of inorganic component. However, if the content of inorganic particles increase further, a dense membrane layer cannot be formed. On the contrary, excessive accumulation of microspheres leads to formation of a large number of empty pores in the membrane, and the membrane structure will become loosen. At the same time, too little content of organic component leads to form a brittle membrane. The above two points lead to a decrease of bonding strength. When the inorganic component content is small, the membrane flexibility increases, but the heat resistance decreases.

![Figure 7. Sketch of the film formation reaction of nano-silicate polymer](image)

4. Conclusion

(1) The initial decomposition temperature of the membrane prepared by sizing agent was 220°C, which was 70°C higher than that of the polyacrylic acid membrane. Organic and inorganic components of the sizing agent are linked in the form of chemical bond, forming a continuous organic-inorganic hybrid network.

(2) The temperature resistance of the fiber treated with sizing agent has been significantly improved. The tensile strength of the coated fiber is 60% higher than that of the uncoated fiber. After 10 h of heat treatment, the strength of the coated fiber is 6 times higher than that of the uncoated fiber, which prove that the film can protect the fiber at the temperature of 340°C.

Acknowledgments

Authors wish to acknowledge the supplyment of basalt fibers by Shanxi BASALT Technology Co., Ltd.
References

[1] Fiore V, Scalici T, Di Bella G, et al. 2015 Composites Part B: Engineering 74 74-94
[2] Li J J, Meng Y, Liu Y C 2011 Advanced Materials Research 239-242 1376-1381
[3] Cory High, Hatem M Seliem, Adel El-Safty, et al 2005 Construction and Building Materials 96 37-46
[4] Militky J K Vladimir 2000 Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals 354(1) 55-62
[5] Shayed M A, Hund R D, Cherif C 2014 Fibers and Polymers 15(10) 2086
[6] Zhao Y, Liu F, Lu J, et al 2017 Fibers and Polymers 18(8) 1586-1593
[7] Liu J, Ge H, Chen J, et al. 2012 Journal of Applied Polymer Science 124(1) 864-872
[8] Interaction between carbon fibers and polymer sizing: Influence of fiber surface chemistry and sizing reactivity 2018 Applied Surface Science 439
[9] Wu Q, Li M, Gu Y, Wang S, Yao L. and Zhang Z 2016 Polymer Composites 37 254-261
[10] Chen J, Zhou X, Ge H, Wang D, Liu H and Li S 2016 Polymer Composites 37 334-341
[11] Wang C, Ge H, Liu H and Liang J 2016 Polymer Composites 37 2719-2726