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Tensile behaviors of ECR-glass and high strength glass fibers after NaOH treatment

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Abstract

ECR-glass and high strength glass (S-glass) fibers were treated in 2 mol/l NaOH solution up to 5 h. The strength maintenance ratio and mass loss ratio of the fibers after treatment were investigated. The surface morphologies were characterized using scanning electron microscopy, and changes of chemical composition were analyzed by energy dispersive X-ray spectroscopy and Fourier transform infrared spectrometry. The alkali resistance and tensile strength of the S-glass fibers are higher compared to those of the ECR-glass fibers as they received less alkaline attack because of the more compact SiO_2 network and the formation of a protective layer on the S-glass fiber surface. The S-glass fibers have a higher mass loss due to the smaller diameter and thinner corrosion layer.

Keywords: Glass fibers; Alkali corrosion; Tensile strength; Mass loss; Microstructure

1. Introduction

High performance filaments are widely used as the reinforcement of the composites due to their excellent properties [1–4]. It is accepted that the fibers in the composites can confer strength and rigidity to the weak matrix. Fibers commonly used are glass fibers, ceramic fibers, carbon fibers, etc. The composites fiber reinforced are unavoidably applied in alkaline environments, but they are very sensitive to alkaline corrosion and show limited mechanical properties. Previous publications reveal that the component responsible for corrosion failures in the composites appears to be the fiber rather than the resin, as the resin appears to play a protective role by shielding the fibers from the corrosive environment [5]. Thus, in order to figure out how to improve the alkali resistance of the composites, the fiber behavior during alkaline environment should be understood.

Some studies have been performed on the durability of the E-glass fibers and certain high performance fibers in alkaline environment [6–9]. They suggested that the alkali solution is very aggressive to the fibers' surface, and the corrosion process is the breaking of Si–O bonds in the glass network by hydroxyl ions. However, these experimental studies about the fiber corrosion behavior are not complete because only a few kinds of fibers are systematically compared.

The ECR-glass fiber is a new fiber which is similar to the E-glass fiber but without boron and fluorine, thus having better strength, chemical resistance and temperature resistance [10]. High strength glass fiber (S-glass fiber) is a stronger and stiffer version of the E-glass fiber. It has a higher modulus of elasticity due to high contents of SiO_2 and Al_2O_3. Both the ECR-glass and S-glass fibers are suitable for all the applications that E-glass suits. The research covering the alkaline resistance for the two fibers is limited by far.

In this work, the strength maintenance ratio and mass loss ratio of the ECR-glass and S-glass fibers after NaOH treatment were examined. The surface morphologies and changes of chemical composition were analyzed. The purpose is to investigate the effect of NaOH on the performance of the ECR-glass and S-glass fibers.

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Table 1
Mechanical properties of the ECR-glass and S-glass fibers.

Property	ECR-glass fiber	S-glass fiber
Strength (cN/tex)	43.5	112.9
Elastic modulus (GPa)	70	84
Elongation at failure (%)	4.5	2.4
Filament diameter (μm)	24	14
Yarn fineness (tex)	4800	480

2. Experimental

The materials used for the present investigation are the ECR-glass fibers (produced by Corning Incorporated, US) and high strength glass fibers (S-glass fibers, produced by Nanjing Fiberglass R&D Institute, China). Their basic properties are shown in Table 1.

The two kinds of fibers were treated in NaOH solution with a concentration of 2 mol/l. Before the treatment, fibers were pre-treated in acetone for size removal in order to avoid that the sizing agent influences the measurement results. The experimental temperature during the treatment was kept to be 95 °C, and the treating time ranged from 1 to 5 h. After the treatment, the samples were rinsed four times in deionised (DI) water and dried. The mass losses of fibers after the treatment were examined using an electronic analytical balance with a precision of 0.0001 g. Control specimens were cut at intervals along the roving. Tensile strength test of the fibers before and after the treatment was performed at a crosshead speed of 20 mm/min by using a YG (B) 026H-1000 Bundle Fiber Strength Tester (Wenzhou, China). The distance between the two clampers before the test was maintained to be 100 mm.

The surface morphologies of the ECR-glass and S-glass fibers before and after the treatment were characterized with a FEI-Sirion scanning electron microscope (SEM). To check any significant chemical modification of the fibers, the specimens were analyzed using energy dispersive X-ray spectroscopy (EDX) and TENSOR27 Fourier transform infrared spectrometer (FT-IR).

3. Results and discussion

3.1. Mass loss

Fig. 1 shows the mass loss ratio as a function of treating time for the ECR-glass and S-glass fibers. For both types of fibers, the mass loss ratio increases sharply before 1 h. After 1 h, it changes slowly. Moreover, the mass loss ratio of the ECR-glass fibers first decreases and then increases. On the contrary, it first increases and then decreases for the S-glass fibers. After 5 h, the mass loss ratio of the ECR-glass fibers is much lower than that of the S-glass fibers.

3.2. Strength maintenance ratio

Fig. 2 shows the strength maintenance ratio of the two types of fibers after NaOH treatment. Compared with the original value, the strength of both fibers drops dramatically until 1 h. It reduced to 31% for the ECR-glass fibers, and 51% for the S-glass fibers. After 1 h, the strength of both fibers falls slowly. The strength maintenance ratio of the S-glass fibers is higher than that of ECR-glass fibers. According to the results of Figs. 1 and 2, there is no close relationship between the mass loss ratio and strength maintenance ratio for the two fibers. Since fiber strength is an important parameter that controls the fracture behavior of composites [11], strength maintenance ratio is able to represent the durability of the fibers. Therefore, the alkali resistance of the S-glass fibers should be higher compared to that of the ECR-glass fibers. One of the reasons may be that the density of framework (mainly composed of Si and Al) for the S-glass fibers is higher than that for the ECR-glass fibers.

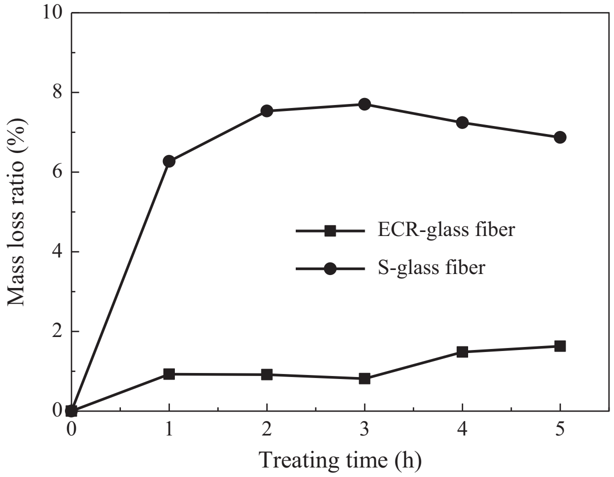

Fig. 1. Mass loss ratio of the fibers as a function of treating time.

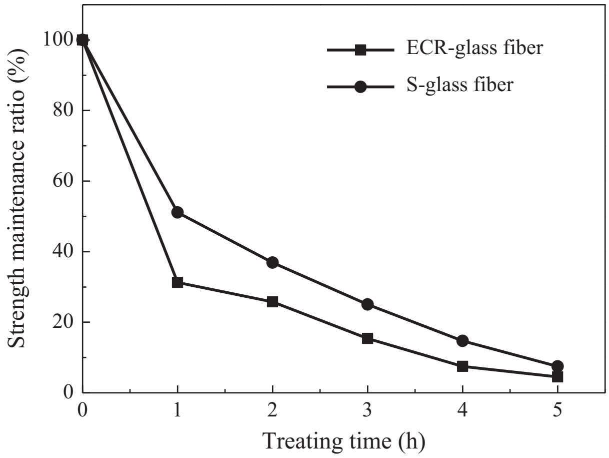

Fig. 2. Strength maintenance ratio of the fibers as a function of treating time.

It is known that the glass fiber corrosion in alkaline media is mainly controlled by dissolving the SiO_2-network. The hydroxyl ions of the solution may disrupt the siloxane bonds in the glass [8,9,12], as shown below:

$$[-\text{Si–O–Si}-]+\text{OH}^- \rightarrow [-\text{Si–OH}]+[-\text{SiO}]^- \quad (1)$$

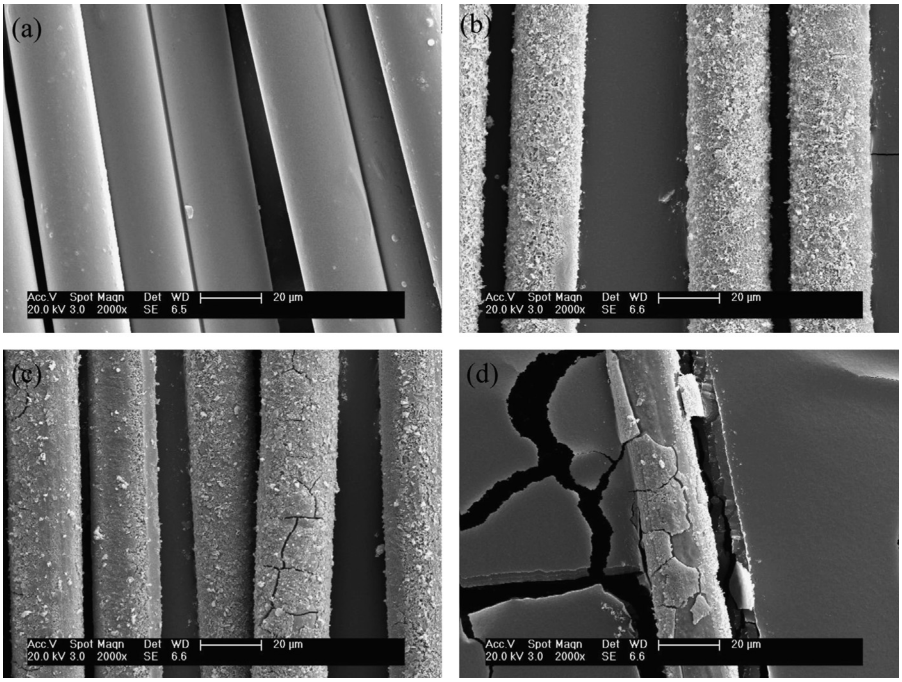

Fig. 3. SEM images of ECR-glass fibers before and after treatment in NaOH solution: (a) original fiber, (b) after 1 h treatment, and (c, d) after 5 h treatment.

Thus the strength of the fibers after treatment in alkali solution is decreased considerably. The S-glass fibers have very integrated and compact SiO_2 network due to high contents of SiO_2 and Al_2O_3. Even though the hydroxyl ion can break the Si–O–Si linkage in NaOH solution, there should be munificent SiO_2-network remained. Therefore, the S-glass fibers have higher strength maintenance ratio after NaOH treatment. Nevertheless, the contents of SiO_2 and Al_2O_3 in the ECR-glass fibers are lower, thus the amount of SiO_2 network reserved should not be munificent in the ECR-glass fibers after alkali corrosion. Consequently, the strength maintenance ratio of the ECR-glass fibers is lower after NaOH treatment.

3.3. *Microstructure*

Fig. 3 shows the SEM images of the ECR-glass fibers before and after NaOH treatment. Before the treatment, the surfaces of the fibers are very smooth although some fibers display surface defect, probably due to abrasion during the manufacturing (as shown in Fig. 3(a)). After 1 h treatment, the glass fiber surface becomes rough due to chemical interactions and it is covered by reaction products. The corrosion products have an amorphous or gel-like appearance. With the treatment time increasing, the thickness of the corroded layer increases. After 5 h treatment, there are some cracks on the corroded layer (see Fig. 3(c)), and some parts of the layer are separated from the fiber surface (see Fig. 3(d)). The EDX analysis results of the fiber surface (Fig. 3) are given in Table 2. Before 1 h, the concentrations of Si and Al of the fiber surface drastically reduce, whereas the Ca content increases. Then the contents of Si, Al and Ca slightly decrease with increasing treatment time. After 5 h, the contents of Si, Al, and Ca are 45%, 6.4% and 44.4%, respectively.

Table 2
The EDX results of ECR-glass fiber surface before and after NaOH treatment (wt%; *n.* = not detectable).

Element	Si	Al	Ca	Mg	K	Na
Original fiber	50.2	8.8	37.3	3.0	0.4	0.3
After 1 h treatment	45.7	7.1	44.6	2.6	*n.*	*n.*
After 5 h treatment	45.0	6.4	44.4	4.2	*n.*	*n.*

Fig. 4 shows the SEM images of the S-glass fibers before and after NaOH treatment. The EDX results of the fiber surface (Fig. 4) are given in Table 3. There is a corroded layer on the surface of the S-glass fibers after NaOH treatment which is as same as the ECR-glass fibers. The thickness of corroded layer also increases with increasing treatment time. Compared with the ECR-glass fibers, the corroded layer is thinner. From the EDX results, a decrease in Si and an increase in Mg contents are observed in the corroded layer, whereas the Al content stays the same. After 5 h treatment, the contents of Si, Al and Mg are 52.5%, 19.4% and 28.1%, respectively.

Although the chemical composition of the fibers is different, both the fibers should react in a similar way. Therefore, it can be deduced that the formation of corrosion layer is typical for the treatment in NaOH solution. Some alkali metal released by the glass through a network breakdown, is partly retained by adsorption at the surface and formed corrosion layer. Taking into consideration the high amount of Ca in the ECR-glass fibers, a passivation Ca–Si-layer was formed on the fiber surface. For the S-glass fibers, an insoluble Si–Mg–Al-layer was formed on the fibers because they have high concentrations of Mg and Al. The corrosion layer becomes more thick and compact with increasing treatment time, which may delay

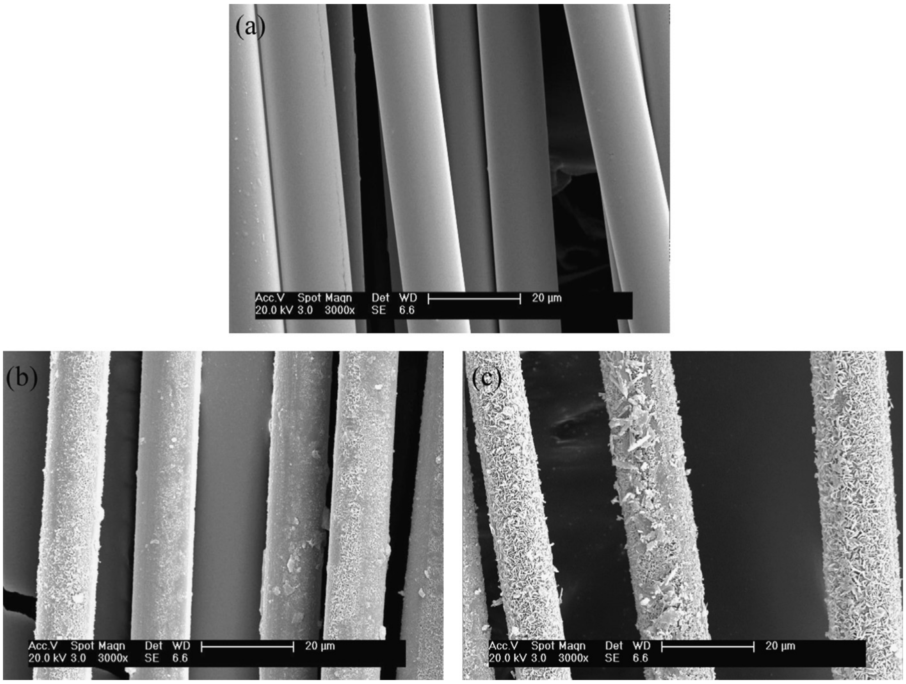

Fig. 4. SEM images of S-glass fibers before and after treatment in NaOH solution: (a) original fiber, (b) after 1 h treatment, and (c) after 5 h treatment.

Table 3
The EDX results of S-glass fiber surface before and after NaOH treatment (wt%; *n.* = not detectable).

Element	Si	Al	Mg	Na
Original fiber	67.4	19. 6	12.9	0.1
After 1 h treatment	62.6	19.4	17.9	0.1
After 5 h treatment	52.5	19.4	28.1	*n.*

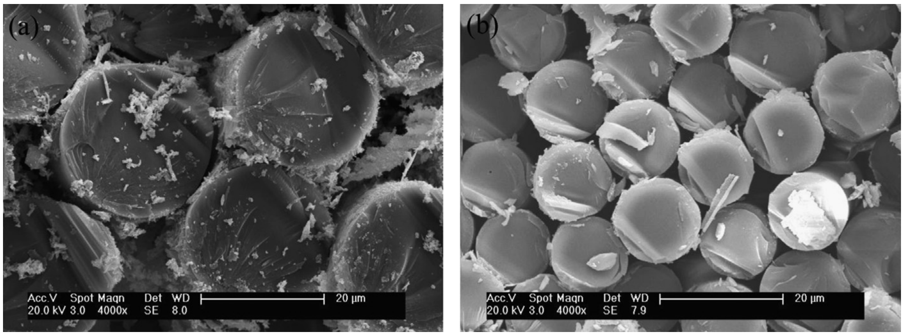

Fig. 5. SEM images of the fiber cross-sections after 5 h treatment in NaOH solution: (a) ECR-glass fiber and (b) S-glass fiber.

the alkali corrosion for the fibers. As the water molecules continue to penetrate into corrosion layer and some alkali metal releases, the corrosion layer expands and is scaling off the fiber finally. The corrosion process is put to the next circulation [12].

Fig. 5 shows the SEM images of the fiber cross-sections after 5 h treatment in NaOH solution. Apparently, the ECR-glass fibers have bigger diameter and thicker corrosion layer compared to those of the S-glass fibers, which probably lead to lower mass loss. From Fig. 5 we also can see that the corrosion layer of the ECR-glass fibers is brittle, which is partially peeled off in several areas. On the contrary, the corrosion layer of the S-glass fibers looks relatively tough. Thus, it is possible that the corrosion layer on the S-glass fibers can provide longer protection than that on the ECR-glass fibers.

3.4. Infrared spectra analysis

To check whether there is framework damage during the treatment, the infrared spectra analysis was performed. Fig. 6 shows the FT-IR spectra of the ECR-glass and S-glass fibers before (upper curves) and after (lower curves) 5 h treatment in

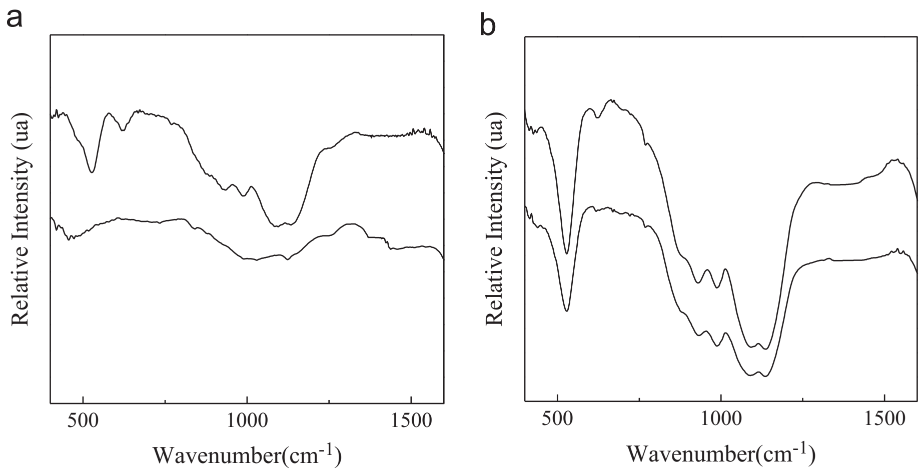

Fig. 6. FT-IR spectra of two fibers before (upper curves) and after (lower curves) 5 h treatment in NaOH solution: (a) ECR-glass fiber and (b) S-glass fiber.

NaOH solution. There are three obvious absorption bands in the spectra for the two fibers before the treatment. The strong band attributed to Si–O is Si–O–Si stretching at around 1100 cm^{-1} [13]. The weak absorption band at around 620 cm^{-1} is assigned to O–Si–O stretching in [SiO_4] or O–Al–O stretching in [AlO_4] [14]. A strong absorption peak at about 434–547 cm^{-1} is due to Si–O–Si or Al–O–Al bending vibrations [15,16]. The absorption peaks related to Si–O–Si and/or Al–O–Al decreased in intensity after 5 h NaOH treatment. It indicated that the SiO_2-network is partially destroyed for both fibers after the alkali corrosion. Since SiO_2 act as glass structure formers, their depletion can disturb the glass structure, therefore reducing the strength of the fibers. Meanwhile, aluminum ions can either occupy the holes between the SiO_4 tetrahedra or join the SiO_2-network to act as part of the glass matrix [17,18]. Its depletion can also disrupt the continuity of the SiO_2-network, further resulting in the fiber strength reduction. In addition, the decline changes of the absorption peaks of the S-glass fibers are much smaller than that of the ECR-glass fibers. It may be explained by less alkaline attack because of the more compact SiO_2 network and forming a protective layer on the S-glass fiber surface.

4. Conclusions

The ECR-glass and S-glass fibers would be damaged greatly in 2 mol/l NaOH solution. The tensile strength of both fibers decreases with increasing treatment time. There are different corrosion product layers on the surfaces of two fibers due to different chemical compositions. A Ca–Si-layer was formed on the ECR-glass fibers, and a Si–Al–Mg–layer was formed on the S-glass fibers. Based on microstructure and FTIR analysis, hydroxyl ions can disrupt the continuity of the glass network, thus reducing the fiber strength. The alkali resistance of the S-glass fibers is higher than that of the ECR-glass fibers as they received less alkaline attack because of the more compact SiO_2 network and forming a protective layer on the S-glass surface.

The results indicate the better alkali resistance of the S-glass fibers and thus point out their potential in future design of composite materials.

Acknowledgments

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