A Comparison of Two Different Surface Modifications on the Properties of Poly (p-phenylene benzobisoxazole) Fibers

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Abstract. Poly (p-phenylene benzobisoxazole) (PBO) fibers were modified by coupling agent 3-Glycidoxypropyltrimethoxysilane (KH-560) and polyphosphoric acid (PPA) respectively. The influence of two treatments on the properties of PBO was investigated, including surface morphology, water absorption and breaking strength retention ratio. The results indicate that the surface roughness of PBO fibers can be increased by both KH-560 and PPA. With the increase of PPA mass fraction, the retention rate of breaking strength of PBO fibers gradually was decreased, and the water absorption rate was gradually increased. Notably, KH-560 can effectively improve the water absorption rate without deteriorating mechanical properties of PBO fibers simultaneously. Compared to treatment by PPA, KH-560 has a milder effect on the performance of PBO fibers, which makes it easier to control the degree of surface modification.

1. Introduction
Poly (p-phenylene benzobisoxazole) (PBO) fibers are known as “super fiber of 21st century” due to the highest strength and module among all commercial synthetic fibers\cite{1}. PBO fibers possess of excellent performances such as superior mechanical properties, good heat resistance and flame retardant, which shows a great potential application in the filed of aerospace and military. However, the lack of chemical active groups leads to chemical inertness and poor interfacial adhesion between PBO fibers and resin, which has highly restricted the use of PBO fibers\cite{2,3}. Thus, to improve the wettability and adhesive property of PBO fiber surface is of great importance for the application of PBO fiber in advanced composites. Herein, various surface modifications have been employed to enhance surface activity of PBO fibers, including acid treatment, coupling agent treatment, copolymerization modification, irradiation treatment, plasma treatment and enzyme treatment\cite{4-9}. Each method has its own advantages and disadvantages, so choosing proper surface treatment is the key of preparing PBO fiber composite.

Given the convenience and efficiency of coupling agent KH-560 and polyphosphoric acid (PPA) to improve surface activity of PBO fibers, they were used to modify PBO fibers respectively in our work. The effects of PPA and KH-560 on the hydrophilic and mechanical properties of PBO fibers were
investigated. By comparison, advantages and disadvantages of two surface modifications were also disclosed, which will provide reference for the study of PBO fibers as reinforced material in the preparation of resin matrix composites.

2. Experimental

2.1. Material
Poly (p-phenylene benzobisoxazole) (PBO) fibers were purchased from Toyobo Ltd. Coupling agent KH-560 was provided by Shanghai Yi Ji Industrial Co. Ltd. Polyphosphoric acid (PPA) was obtained from Aladdin Chemical Reagent Co. Ltd. Acetic acid and ethanol were supplied by Sinopharm Chemical Reagent Co. Ltd.

2.2. Surface modification by KH-560
Prior to use, PBO fibers were immersed in absolute ethanol for 1h under ultrasonic vibration. After soaking for 24h, PBO fibers were washed by distilled water and then were dried at 120°C for 1h to obtain pretreated PBO fibers. They were then immersed into different mass fraction KH-560/ethanol solution (0%, 5%, 10%, 15%) by ultrasonic for 10 minutes at room temperature, followed by washed with distilled water and dried at 120°C for 1h to obtain KH-560/PBO fibers.

2.3. Surface modification by PPA
The pretreated PBO fibers were immersed into different mass fraction PPA/ acetic acid solution (0%, 5%, 10%, 15%) and PPA/ethanol solution (0%, 5%, 10%, 15%) respectively for 5min at room temperature. Weak base solution was used to neutralize excess residual acid. After that, PBO fibers were washed with distilled water and dried at 120°C for 1h to finally obtain PPA/PBO fibers.

2.4. Characterization
Scanning electron microscope (SEM) morphologies of the samples were analyzed by SIRION2000 (FEI, Holland). The samples were sputtered with Au before observation. X-ray photoelectron spectroscopy (XPS) analyses of the elemental chemical composition of PBO fibers before and after treatment were carried out by ESCALAB250XI XPS (ThermoFisher Scientific, America). Breaking strength of the samples before and after treatment was measured by MTS-810 electronic universal material testing machine (MTS Systems Co, China) following ASTM D 3379-15 at room temperature and 30 specimens were tested to obtain the average. In the case of moisture absorption measurement, each sample was dried in the oven for 1h. The dried samples were immersed in the distilled water for 3h until the fibers reached to moisture absorption balance. The water absorption Ma was calculated using:

\[ M_a = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \]

2.4.1. where Mdry and Mwet are, respectively, the mass of the dried sample and the mass of the wet sample. For each sample, three repeated experiments were taken to ensure reliability of the results.

3. Result and discussion
The surface chemical compositions of pristine PBO fibers, KH-560/PBO fibers and PPA/PBO fibers were assessed by XPS as shown in Fig 1. The X-ray photoelectron spectroscopy of PPA/PBO fibers was basically unchanged from that of pristine PBO fibers without modification. Notably, it was found that a new peak emerged at 102eV corresponding to the Si2p in the case of KH-560/PBO fibers, suggesting KH-560 was successfully introduced onto the PBO fiber surface. It results from hydrolysis reaction of KH-560, which was shown in Fig 2. The silicon hydroxyl (-SiOH) formed from (-SiOCH3) during the hydrolysis of KH-560, which is unstable and easy to undergo dehydration condensation reaction with the carboxyl group in the PBO fiber molecule.
Surface elemental compositions of pristine PBO fibers, KH-560/PBO fibers and PPA/PBO fibers were listed in Table 1. The chemical composition of the surface of PBO fiber has changed after surface modification of KH-560 and PPA. After the modification of KH-560, the relative content of carbon and oxygen in PBO fibers was increased, while that of nitrogen was decreased. Due to the hydrolysis reaction of KH-560 discussed above, the relative content of silicon was increased from 0% by 4.3%, which was consistent with results of XPS. Given that the modification by PPA was considered as physical process, there was no element emerged on the surface of PBO fibers. It can also be observed that the relative content of carbon in PPA/PBO fibers was decreased and that of oxygen and nitrogen was increased.

| Sample          | Relative element content (%) |
|-----------------|------------------------------|
|                 | C  | N  | O  | Si |
| Pristine PBO    | 78.6 | 10.7 | 10.7 | 0.00 |
| KH-560/PBO      | 81.1 | 5.2 | 8.9 | 4.3 |
| PPA/PBO         | 72.8 | 14.3 | 12.9 | 0.00 |

The SEM images of pristine PBO fibers and KH-560/PBO fibers were given in Fig 3 to disclose the effect of KH-560 on surface morphology. For pristine PBO fiber (Fig 3a), it is evident that the surface is quite neat and smooth before modification by KH-560. As a comparison, KH-560/PBO fiber was covered with a layer of thin film, that is, the roughness of PBO fibers was increased. This is because silicon hydroxyl (-SiOH) generated after the hydrolysis of KH-560 and then underwent a shrinkage reaction with carboxyl group in the PBO fiber molecule, which formed a deposited layer on the surface of PBO fibers. Meanwhile, as terminal group of KH-560, epoxy groups were exposed to the surface of PBO fibers. The polarity and reactivity of terminal group R in coupling agent are major factors affecting the interfacial strength of PBO fibers. After activated by KH-560, the interfacial adhesion strength of PBO fibers can be improved under the joint action of chemical bonds and physical infiltration, among which chemical bonds play a major role.
Surface morphology of PBO fibers treated with PPA/acetic acid solution or PPA/ethanol solution was shown in Fig 4. It can be seen from the figure that after PPA treatment, the surface of PBO fibers demonstrated different degrees of swelling and etching, and the roughness of PBO fibers was increased. After treatment with PPA/acetic acid solution, the surface PBO fibers is rougher with some deep grooves or surface damage. While the surface roughness of PBO fibers treated with PPA/ethanol solution was increased with only some shallow grooves or fine lines on the surface. It’s well-known that PBO fibers have a skin-core structure. When subjected to an external force, the surface structure of PBO fibers is the main object of the external force load. Therefore, even small regions of the fiber surface damage will lead to a sharp deterioration of mechanical properties of PBO fibers. Since PPA/acetic acid solution is acidic, the surface structure of PBO fibers treated with PPA acetic acid solution was destroyed, and the internal structure of the PBO fibers was also damaged to some extent. The residual PPA/acetic acid solution on the surface was neutralized by weak base, which may also cause further etching or damage to the surface structure of PBO fibers. Partial PPA in PPA/ethanol solution will react with ethanol solution to form a mixed solution of acid, ester and alcohol. The surface layer of PBO fiber swelled and shed under the action of PPA/ethanol solution. Due to the low concentration of PPA, the reaction was quiet mild, thus only relatively uniform and shallow etching appeared on the surface of PBO fibers. Each figure should have a brief caption describing it and, if necessary, a key to interpret the various lines and symbols on the figure.

Figure 4. Effect of different PPA systems on the surface morphology of PBO fibers
PPA / acetic acid (a); PPA / ethanol (b)

The effect of surface treatments on the surface activation of PBO fibers can be indirectly characterized by the measurement of fiber water absorption and the change of fiber hydrophilicity. Fig 5 shows the change of water absorption of PBO fibers treated by varying mass fraction (0%, 1%, 3%, 5%, 7%) of KH-560 or PPA. The curve of water absorption of KH-560/PBO showed an inverted “v” shape with increasing mass fraction of KH-560. The highest water absorption was obtained when the mass fraction of KH-560 reached 3%, that is, the surface of the PBO fibers was maximally activated. In contrast, the water absorption of PPA/PBO was increased along with the concentration of PPA, suggesting higher activation degree of PBO fibers. It can be explained by the fact that the terminal group of KH-560, i.e. epoxy group, was exposed to the surface of PBO fibers, which enhanced the hydrophilicity of PBO fibers. Therefore, within a certain range, as the concentration of the coupling agent increases, more reactive epoxy groups are bonded to the surface of PBO fibers, and the water absorption of PBO fibers gradually is increased. Since the hydrophilicity of PBO fibers was mainly influenced by the single molecular layer of KH-560 deposited on the surface of PBO fibers, as the mass fraction of KH-560 further increased, they may aggregate on the surface of PBO fibers. Consequently, epoxy groups in KH-560 may crosslink with each other and siloxane groups not only deposited on the fiber surface but also tended to gather together due to saturation, leading to lower hydrophilicity and water absorption of PBO fibers. As for PPA/PBO fibers, due to swelling and etching, the surface roughness of PBO fibers was greatly improved, and the water absorption of PBO fibers was also increased. As the mass fraction of PPA increases, the fiber cortex was destroyed and PBO fibers were microfibrillated, so the hydrophilicity and water absorption of PBO fibers continued to be increased.
Figure 5. Water absorption of different concentration of coupling agent

Fig 6 shows the retention ratio of breaking strength of PBO fibers treated with varying mass fraction (0%, 5%, 10%, 15%, 20%) of PPA/acetic acid, PPA/ethanol and KH-560/ethanol solution, respectively. It can be seen from Fig 6 that KH-560 had slight influence on the breaking strength of PBO fibers. However, the breaking strength of PBO fibers rapidly degraded after modification by PPA, especially in the case of treated with PPA/acetic acid solution. This is because KH-560 only deposited on the surface of PBO fibers, without causing damage to chemistry structure of PBO fibers. After modification by PPA/ acetic acid solution, oxazole ring in molecule was broken, highly axis orientation of pristine PBO fibers was disrupted and PBO fibers were microfibrillated, which led to the destruction of compact structure of PBO fibers and a sharp decline in the breaking strength. During the process of treatment with PPA/ ethanol solution, the esterification reaction between PPA and ethanol lowered the concentration of PPA in the solution. The effect of PPA/ ethanol solution was mainly about swelling, which only occurred on the surface of PBO fibers. Therefore, the surface damage degree of PBO fibers modified by PPA/ethanol solution was moderate, and the retention ratio of breaking strength was higher than that of PBO fibers treated with PPA/ethanol solution.

4. Conclusion
In our work, PBO fibers were treated by coupling agent (KH-560) and polyphosphoric acid (PPA) respectively. After surface modification by KH-560 and PPA, the surface morphology of PBO fibers became rougher, that is, the roughness of PBO fibers was increased. And it was found that the surface activity of PBO fibers was significantly improve with increasing mass fraction of KH-560 and PPA. By comparison, KH-560 has a milder effect on the performance of PBO fibers, while PPA can negatively affect the strength of PBO fibers. Thus, for the purpose of avoiding causing damage to internal structure of PBO fibers, it is necessary to strictly control the mass fraction and use time of PPA to reduce the etching degree of PPA on PBO fiber surface.
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