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Tribological properties of oxidation modified carbon fibre–reinforced polyamide 6 composites

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The ozone modification method and air-oxidation were used for the surface treatment of polyacrylonitrile-based carbon fibre. The interfacial properties of carbon fibre–reinforced polyamide 6 (CF/PA6) composites were investigated by means of single fibre pull-out tests. It was found that the IFSS values of the composites with ozone treated carbon fibre are increased by 60% compared with that without treatment. The effect of surface treatment of carbon fibres on the tribological properties of CF/PA6 composites was also investigated for comparison. Experimental results revealed that surface treatment can effectively improve the interfacial adhesion between carbon fibre and PA6 matrix. Thus the wear resistance was significantly improved.

Keywords: *ozone; CF/PA6 composite; single fibre pull-out; interfacial adhesion*

1. Introduction

The application of carbon fibres–polymer composites has been rising during the last decade, mainly in the car and aerospace industry, due to the improvement of the electrical conductivity and mechanical stiffness. Polyamide, due to its unusual properties such as good thermal stability, low electric permittivity, high mechanical strength and chemical inertness, is becoming a strong competitor of matrix in the manufacture of advanced composite materials. Fibre-reinforced polyamide matrix composites with high performance have especial applications in aerospace, robots, sports goods, etc. Carbon fibres possess exceptional specific strength and stiffness, and hence they have important applications in structural composites. The performance of such composites depends on the properties of the fibres which depend not only on the type ofthe manu-

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facturing process [1–3] and the surrounding matrix, but also on the interface between them [4, 5]. However, as a composite material reinforcement, the full potential of carbon fibres has not yet been realized. This is due primarily to fibre–matrix adhesion. In order to harness the properties of carbon fibres and ensure good stress transfer, there must be adequate adhesion between the fibres and the matrix. Consequently, a variety of surface treatments of carbon fibres are developed such as oxidation, coating, grafting [6–11], etc. All surface treatments enhance the interfacial shear strength (IFSS) by introducing chemically active groups on the fibre surfaces which increases the reactivity with the matrix, enhancing surface roughness to produce better mechanical interlocking as well as increasing the surface energy for improved wetting. The ozone modification method is a kind of simple and efficient method for carbon fibre modification.

In this work, the ozone modification method is used for the surface treatment of carbon fibre. The purpose of this study was to examine the influence of ozone surface treatment methods on the interfacial adhesion properties of CF/PA6 composites and the surface characteristics of carbon fibre before and after treatment. And further research on ozone modification method is necessary for the application of this method.

2. Experimental

Materials. For the present investigation, the reinforcement materials were continuous polyacrylonitrile (PAN)-based carbon fibres manufactured by Shanghai Sxcarbon Technology Co. Ltd. prior to use, and polyamide-6 supplied by YueYang Juli Engineering Plastic Co. Hunan with the following properties: tensile strength – 85 MPa, flexural strength – 115 MPa, the density of the matrix – 1150 kg/m^3

Fibre surface treatment. Oxidation of the carbon fibres was carried out at 450 °C in an oxidation furnace for 10 min. The selected oxidation condition has been proved to be the most effective one for this kind of carbon fibre. Ozone surface treatment of the carbon fibres was carried out in a XFZ-5BI generator for 3 min [12]. The concentration was 10–36 mg/dm^3.

Single fibre pull-out test. A microbond test was performed to evaluate the interfacial shear strength (IFSS) between carbon fibre and matrix by pulling out a fibre from a PA6 resin droplet. The composite specimens were prepared by a screw in-line type injection moulding machine with the help of a special embedding machine, in which the fibre can be embedded perpendicular to the surface of the matrix globe with a defined embedded length.

The sample for the single fibre pull-out measurement is a few millimetres long fibre, partly embedded at one end in a polymer and orientated perpendicular to the polymer surface (Fig. 1). On a metal surface a small amount of polymer in the form of a hemisphere supported a vertically positioned fibre, which was embedded by using a special embedding machine [13]. The embedding depth of the carbon fibre filament in the PA6 resin was 105 μm, which is ca.15 times the size of the fibre diameter(7μm).This makes it possible to ensure that the stress distribution around the fibre–matrix interface is nearly homogeneous.

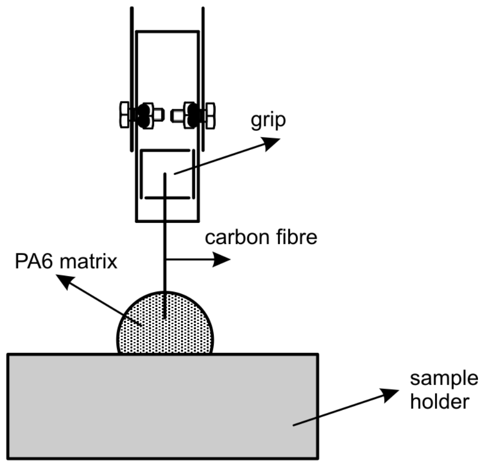

Fig. 1. Single fibre pull-out model

The pull-out test was performed at a crosshead displacement rate of 0.5 $\mu m\cdot s^{-1}$. The value of IFSS was calculated according to the equation

$$\mathrm{IFSS} = \frac{F}{\pi dl}$$

where F is the maximum load, d – the diameter of the carbon fibre, l – the length of the fibre embedded in the resin. The recorded value of IFSS was calculated from the normal distribution of more than 10 successful measurements

Friction and wear tests. Friction and wear tests were done using a ball-on-block reciprocating UMT-2MT tribometer at room temperature with a relative humidity of 45–55%. The specimen disks, cut from the above sintered composites, were 30 mm long, 20 mm wide and 5 mm thick. The disks were polished using a fine grade SiC emery paper and cleaned ultrasonically with acetone and dried before testing. The counterpart was a GCr15 steel ball of the hardness HRC61 and surface roughness Ra ca. 0.05 μm with the diameter of 3 mm. The reciprocating friction stroke was 5 mm and tests were conducted at a normal spring-driven load. The test duration was 2 h and the friction coefficient was taken to be the average value of the whole process. During tests, the friction coefficient was continuously measured using a load cell. The cross-section of the wear scars were measured using a surface profilometer (model 2206, Harbin Measuring and Cutting Tool Group Co. Ltd., China). The wear volume of the specimen was calculated from the equation $V = Sl$, where V is the wear volume in m^3, S is the cross-section area, l is the length of the stroke. The specific wear rate of the composite was calculated using the equation $K = V/LF$, where V is the wear volume [m^3], L is the sliding distance [m], F is the applied load [N]. Five tests were conducted under each test condition and the average values of the measured friction coefficient, and the specific wear rate were used for further analysis. The worn surfaces of CF/PA6 composites were investigated with a scanning electron microscope (SEM).

Preparation process. The hot moulding technique was employed to fabricate composite specimens, which is the most common technique for the sintering of pure PA6 without any sintering aids. In this process, the filler carbon fibres and the PA6 were churned together in a mixer. Mixing was done for a few minutes at the addition of each component for about 20 min. Sintering powder (20 vol. % of carbon fibres and 80 vol. % of PA6) was placed inside a stainless mould with its inner walls coated with a BN slurry to avoid any interaction between the powder and steel and also to facilitate the demoulding process. The compounds were put into the QLB-D170×170 vulcanizing machine at 280 °C for 1 h under a constant pressure of 12 MPa, then heated from 280 °C to 340 °C in 1 h. When the temperature reached 340 °C, it remained constant for 1 h. Then the compounds were cooled from 340 °C to 200 °C in 70 min. During the whole process, the pressure of ozone was constant. The obtained materials were then cooled to room temperature to get the composites.

3. Results and discussion

3.1. IFSS of CF/PA6 composites

Figure 2 shows that the IFSS values of the composites with ozone treated carbon fibre are increased by 60% compared with those without treatment. It is proved that the better interfacial adhesion can be obtained through surface modification.

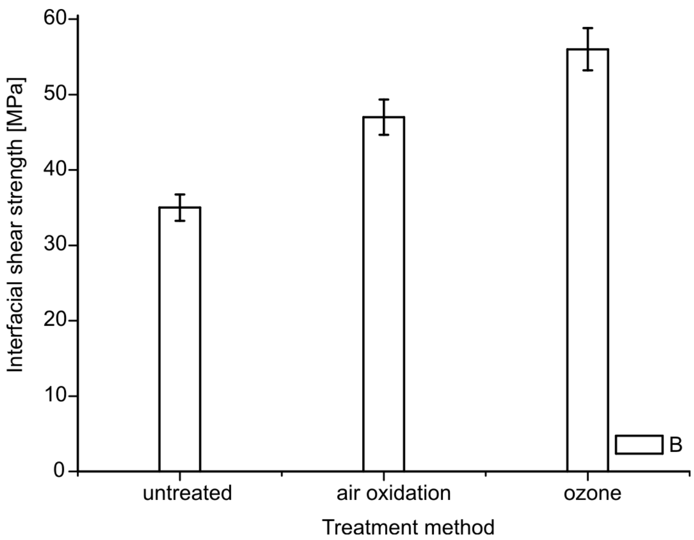

Fig. 2. IFSS of CF/PA6 composites

The reasons attributed to this is that the ozone treatment is a method to bind oxygen functional groups on carbon fibre surfaces, which increase the interlock between the fibre and matrix, leading to the increase of the IFSS of composites, which can effectively transfer the stress from matrix to the fibre, thus the fibre can provide more reinforcement. Therefore, the IFSS of the composite reinforced by ozone treated carbon fibres are considerably improved.

3.2. Friction and wear properties

Figure 3 shows the variation of the friction coefficient of the CF/PA6 composites with load. The friction coefficient of all PA6 composites increases as the load increases from 6 N to 15 N under the same reciprocating sliding frequency 8 Hz. This can be explained by the friction-induced thermal and mechanical effects, which may increase the actual contact area between the frictional pair as the load increases. Changes in the friction coefficient of CF/PA6 composites with reciprocating sliding frequency are shown in Fig. 4. The friction coefficient decreases as the reciprocating sliding frequency increases from 1 Hz to 12 Hz under the same load of 12 N. This was attributed to the increased softening and plastic deformation of the polymer matrix which was caused by the increased reciprocating sliding frequency. The ozone treated CF/PA6 composite exhibits the lowest friction coefficient and the untreated PA6 composite exhibits the highest friction coefficient both under the same reciprocating sliding frequency (Fig. 3) and at the same load (Fig. 4). The modification of the carbon fibres strengthens the combination of the interface between the fibres and the PA6 matrix and increases the elastic modulus of the PA6 composites. This will be the reason why the friction coefficient of the modified carbon fibre reinforced PA6 composites is reduced.

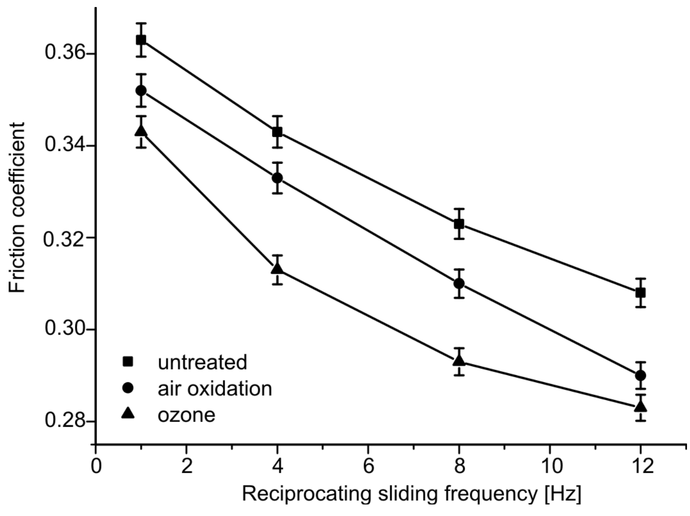

Fig. 3. Dependences of the friction coefficients on load for the PA6 composites

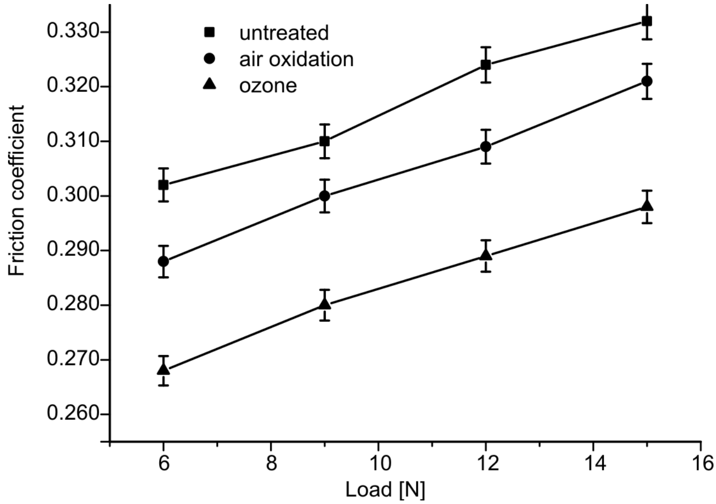

Fig. 4. Dependences of the friction coefficients
on reciprocating sliding frequency for the PA6 composites

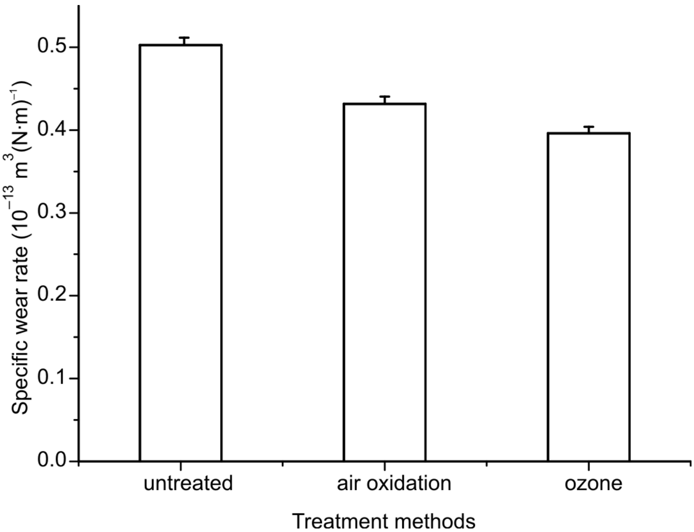

Fig. 5. Specific wear rate of PA6 composites under the load of 12 N
and a reciprocating sliding frequency of 8 Hz

Figure 5 gives the specific wear rate of three CF/PA6 composites under the load of 12 N and reciprocating sliding frequency of 8 Hz. It is seen that the untreated composite has the highest specific wear rate, while the ozone treated composite has the lowest one. The specific wear rate itself depends on the properties of the filler, of the matrix and of the filler/matrix bond strength. In addition, the relative hardness of the filler to that of the counterface, the content, shape, size, distribution and orientation of the filler, and the abrasiveness of filler against the matrix are important parameters. In this system, the difference of specific wear rate mainly comes from the bond strength between the reinforcement and the matrix. It can be seen from Fig. 5 that the modification of the carbon fibres can improve the wear resistance of the PA6 composites, reflecting the effectiveness of the modification of the carbon fibres on increasing the combining strength of the interface between the carbon fibres and PA6 matrix. The above experimental results reveal that ozone treatment greatly improves the friction-reducing and wear-resistance properties of PA6 composite under dry sliding conditions.

The normal load and reciprocating sliding frequency were fixed at 12 N and 8 Hz, respectively. SEM images of the worn surfaces of PA6 composites filled with carbon fibres that had been subjected to different surface treatments are shown in Fig. 6.

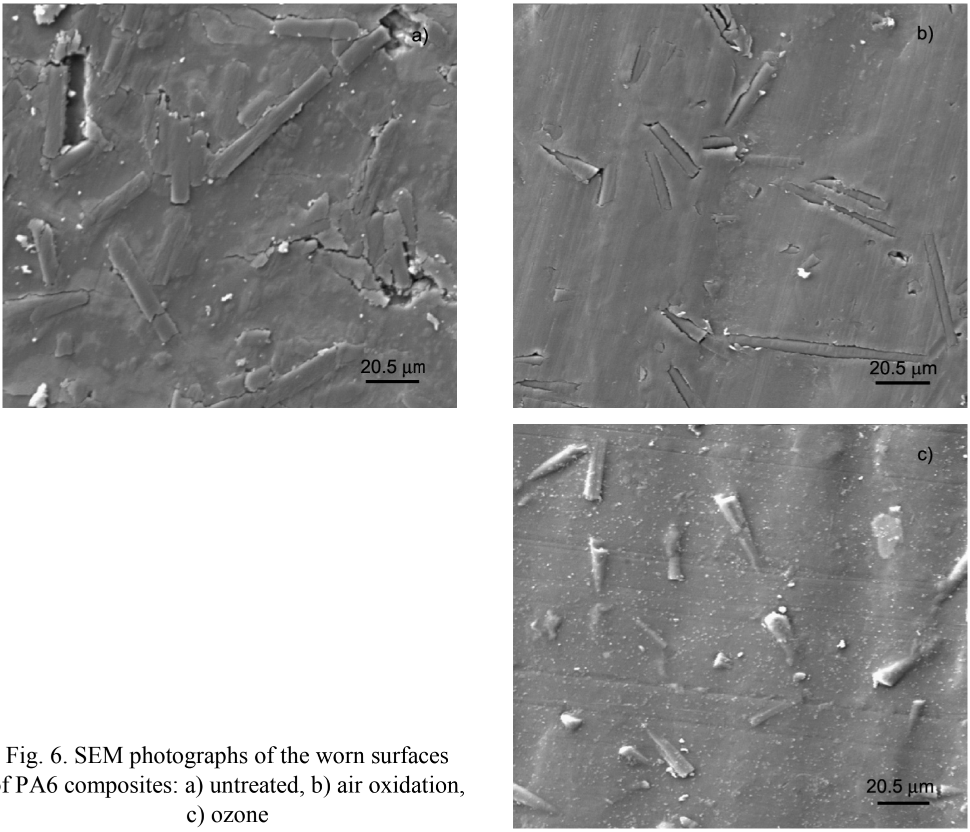

Fig. 6. SEM photographs of the worn surfaces of PA6 composites: a) untreated, b) air oxidation, c) ozone

For the PA6 composite filled with untreated carbon fibres, there are many cracks located near the carbon fibres, as shown in Fig. 6a. Deep pores exist between carbon fibres and PA6 matrix, which indicates that there is a very poor interfacial adhesion between the fibre and the PA6 matrix. Thus the untreated fibres are more prone to be peeled off due to the weak interface bonding. The fillers are easily detached from the matrix under the load of 12 N leaving cavities whose boundaries are the same shape as the filler fibres removed. Many cavities within the matrix material structure lead to stress concentrations in the matrix resulting in higher local stress, microcracking, and in consequence a high specific wear rate. Furthermore, the detachment of fillers causes the adjacent matrix to be poorly supported and hence is subjected to greater stress and thus is more susceptible to fracture. Therefore, the load-carrying capability of the composite is reduced, resulting in a decrease in the/its wear resistance property.

On the worn surfaces of the PA6 composites containing the modified fibres, the damage became weaker, indicating how effectively surface modification of carbon fibres improves the wear resistance of the PA6 composites, as shown in Figs. 6b, c. For the air oxidated CF/PA6 composite, the worn surface is smoother than the untreated one, as seen in Fig. 6b. There are also pores between carbon fibres and PA6. This indicates that the interfacial adhesion between carbon fibres and PA6 is not strong enough, even though carbon fibres are air oxidated. Poor interaction leads to high abrasion wear due to the ease of fibre cracking or displacement. The reinforcing fibres are apt to be pulled-out if the resultant force of applied load and friction force exceeds the interface bonding strength during wear. Microcracks are observed at the surface either at the fibre–matrix boundary or at weak spots in the matrix and eventually lead to delamination of the matrix material. Poor adhesion of the filler to the matrix gave rise to the initiation of these cracks and hence increased the wear rate [12]. Probably, a crack follows the fibre–matrix interface and passes between the fibres at their closest distance. The crack propagates under the original surface matrix layer and causes fragments of the matrix to be broken off, leaving the fibres bare. The driving force for the crack comes from the friction forces being applied on the matrix surface. Where the fibres are close to each other the matrix between the fibres are often fragmented and broken off when the crack propagates along the fibre surface. Additionally, the cavity shown in the PA6 matrix is the result of a filler carbon fibre detaching from the matrix due to loss of matrix around it and poor adhesion between the filler and matrix.

For the composite filled with ozone treated carbon fibres, as shown in Fig. 6c, the worn surface is quite smooth and no cracks are visible. CF and PA6 are compactly bonded and no pores exist between the fibre and the matrix. This indicates that the filler carbon fibres in ozone treated CF/PA6 have good bonding to the matrix and support the load from the counterbody effectively. The carbon fibres are not easily detached from the PA6 matrix in the friction process, due to the improvement in the interfacial adhesion between the carbon fibres and PA6 matrix after ozone treatment. Thus, the load is effectively supported by carbon fibres and the large-scale transfer and rub off of PA6 will be restrained. Accordingly, the wear of the PA6 composite filled with ozone treated carbon fibres was reduced.

4. Conclusions

The effect of ozone treatment has been investigated on interfacial and tribological properties of carbon fibre–reinforced PA6 composites. The IFSS of the composites were improved by ozone treatment. Ozone treatment effectively promotes the interfacial adhesion between the carbon fibre and PA6 matrix. IFSS values of the composites with ozone treated carbon fibre are increased by 60% compared with those of untreated composites. The friction coefficient and specific wear rate of CF/PA6 composite can be decreased after surface treatment of carbon fibres. The ozone treated composite has the lowest friction coefficient and specific wear rate under a given applied load and reciprocating sliding frequency.

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