Effect of Fiber Surface Treatment
on Wear Characteristics of
Carbon Fiber Reinforced Polyamide 6 Composites

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ABSTRACT: *Ozone modification method and air-oxidation were used for the surface treatment of polyacrylonitrile(PAN)-based carbon fiber. The surface characteristics of carbon fibers were characterized by X-ray photoelectron spectroscopy (XPS). The interfacial properties of carbon fiber reinforced polyamide 6 (CF/PA6) composites were investigated by means of the single fiber pull-out tests. As a result, it was found that IFSS values of the composites with ozone treated carbon fiber are increased by 60% compared to that without treatment. XPS results show that ozone treatment increases the amount of carboxyl groups on carbon fiber surface, thus the interfacial adhesion between carbon fiber and PA6 matrix is effectively promoted. The effect of surface treatment of carbon fibers on the tribological properties of CF/PA6 composites was comparatively investigated. Experimental results revealed that surface treatment can effectively improve the wear resistance of CF/PA6.*

KEY WORDS: *Ozone, CF/PA6 composite, Single fiber pull-out, Interfacial adhesion.*

INTRODUCTION

The application of carbon fibers/polymer composites has continuously risen during the last decade, especially in 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 dielectric constant, high mechanical strength and chemical inertness, is becoming a strong competitor of matrix in the manufacture of advanced composite materials. The fiber-reinforced polyamide matrix composites with high performance have special application in aerospace, robots, sports goods, etc.

Carbon fibers possess exceptional specific strength and stiffness and hence they find important applications in structural composites. The performance of such composites depends on the properties of the fibers due to the manufacturing 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 fibers has not yet been realized. This is due primarily to fiber/matrix adhesion. In order to harness the properties of carbon fibers and ensure good stress transfer, there must be adequate adhesion between

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the fibers and the matrix. Consequently, a variety of surface treatments of carbon fibers 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 fiber 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. Ozone modification method is a kind of simple and efficient method for carbon fiber modification.

In this work, ozone modification method is used for the surface treatment of carbon fiber. 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 fiber before and after treatment. And further research on ozone modification method is necessary for the application of this method.

EXPERIMENTAL SECTION
Materials

For the present investigation, the reinforcement materials were continuous polyacrylonitrile(PAN)-based carbon fibers manufactured by Shanghai Sxcarbon Technology Co. Ltd . Prior to use, the fiber surfaces were cleaned by acetone. Polyamide-6 supplied by YueYang Juli Engineering Plastic Co. Hunan with the following specified properties: tensile strength, 85 MPa; flexural strength, 115 MPa; density, 1150 kg/m^3; MFI of 1.95dg/min at 230°C; melting point 225°C was used as the matrix.

Fiber surface treatment

Oxidation of the carbon fibers was carried out at 450 °C in oxidation furnace for 10 minutes. The selected oxidation condition has been proved to be the most effective one for this kind of carbon fiber [12]. Ozone surface treatment of the carbon fibers was carried out in XFZ-5BI generator (Tsinghua University) for 3 minutes [12]. The concentration is 10-36 mg/L.

Single fiber pull-out test

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

The sample for the single fiber pull-out measurement is a few millimeters long fiber, which is partly embedded at one end in a polymer and is orientated perpendicular to the polymer surface. On a metal surface a small amount of polymer in the form of a hemisphere carried the vertically positioned fiber, which is embedded by using special embedding machine [13]. For all the experimental in this study, the PA6 resin on carbon fiber monofilament had the embedded length of 105μm around 15 times of the fiber diameter (7μm). So that it was possible to get nearly equal stress distribution around the fiber/matrix interface.

The pull-out test was performed at a crosshead displacement rate of 0.5 μms^{-1}. The recorded value of IFSS was calculated from the normal distribution of more than 10 successful measurements

XPS analysis of the carbon fiber surfaces

The chemical composition changes of the CF surfaces were analyzed by XPS (PHI-5702). The spectra were collected using a 250-W Al Ka line (hv = 148616eV). The C1s electron binding energy was referenced at 284.6 eV.

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 in length, 20 mm in width and 5 mm in thickness. 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 hardness HRC61 and surface roughness Ra about 0.05 μm with a 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 hours and the friction coefficient was 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 & Cutting
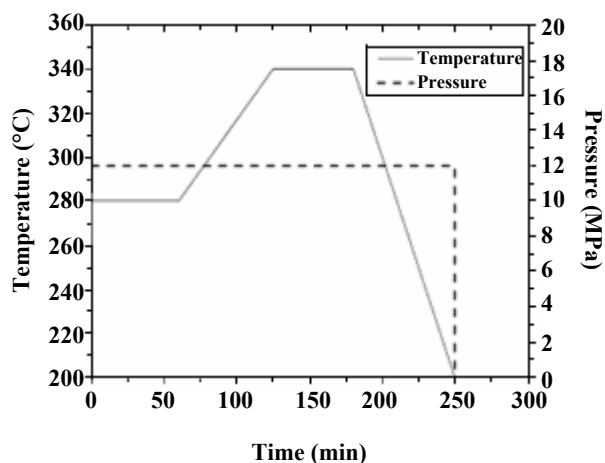
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Fig. 1: The change of temperature and pressure with time.

Fig. 2: IFSS of CF/PA6 composites.

Tool Group Co. Ltd., China). The wear volume of the specimen was calculated using the equation V=Sl, where V is the wear volume in m^3, S is the area of cross-section, l is the length of the stroke. Specific wear rate of the composite was calculated using the equation of 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 measured friction coefficient, specific wear rate were used for further analysis. The worn surfaces of CF/PA6 composites were investigated with scanning electron microscope (SEM, Multimode Nanoscope IIIa, Veeco, France).

Preparation process

The hot moulding technique was employed to prepare the composite specimens, which is the most common technique for the sintering of pure PA6 without any sintering aids. In this process, the filler carbon fibers 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 minutes. Sintering powder (20 vol% carbon fibers and 80 vol% 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 the temperature 280 °C for 1 hour with the constant pressure 12 MPa, then heated from 280 °C to 340 °C with the heating rate of 60°C/h in 1 hour. When the temperature reached 340 °C, the temperature remained constant for
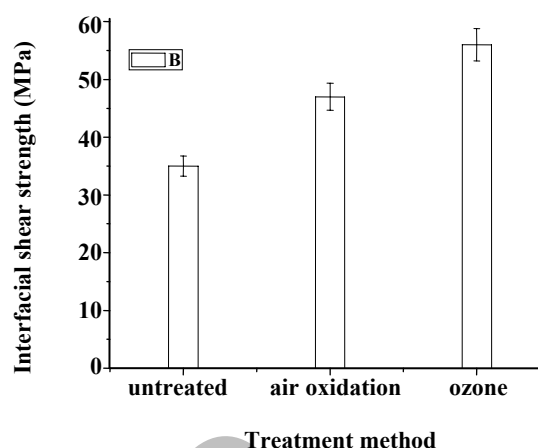
1 hour. Afterwards the compounds were cooled from 340 °C to 200 °C with the cooling rate of 120 °C /h in 70 minutes. During the whole process, the pressure was constant. The compounded materials were then cooled to room temperature to get the composites. The sintering cycle can be visualized with the help of Fig. 1.

RESULTS AND DISCUSSION

IFSS of CF/PA6 composites

Fig. 2 shows that the IFSS values of the composites with ozone treated carbon fiber are increased by 60% compared to that without treatment. It is proved that the better interfacial adhesion can be obtained through surface modification. The reasons attribute that the ozone treatment was used as a method to bind oxygen functional groups on carbon fiber surfaces, which increase the interlock between the fiber and matrix, leading to the increase of the IFSS of composites, which can effectively transfer the stress from matrix to the fiber, so the fiber can bring more reinforcement. Therefore, the IFSS of the composite reinforced by ozone treated carbon fibers are considerably improved.

Friction and wear properties

Fig 3 shows variation of the friction coefficient of the CF/PA6 composites with load. It is seen in Fig. 3 that 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

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between the frictional pair as the load increased. Changes of 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 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 fibers strengthens the combination of the interface between the fibers 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 fiber reinforced PA6 composites is reduced.

Fig 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. 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 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 fibers can improve the wear resistance of the PA6 composites, reflecting the effectiveness of the modification of the carbon fibers on increasing the combining strength of the interface between the carbon fibers 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 condition.

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 differently surface treated carbon fibers are shown in Fig. 6. For the PA6 composite filled with untreated carbon fibers, there are many cracks located near the carbon fibers.
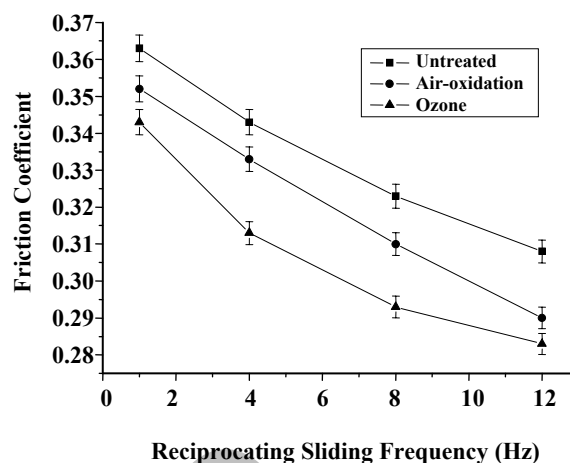

Fig. 3: Variations of friction coefficient with load for the PA6 composites.
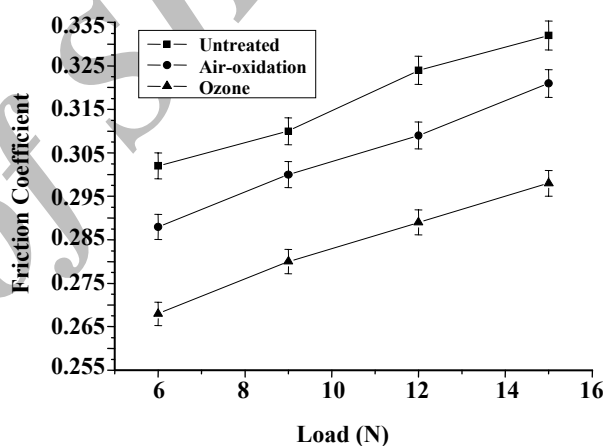

Fig. 4: Variations of friction coefficient with reciprocating sliding frequency for the PA6 composites.
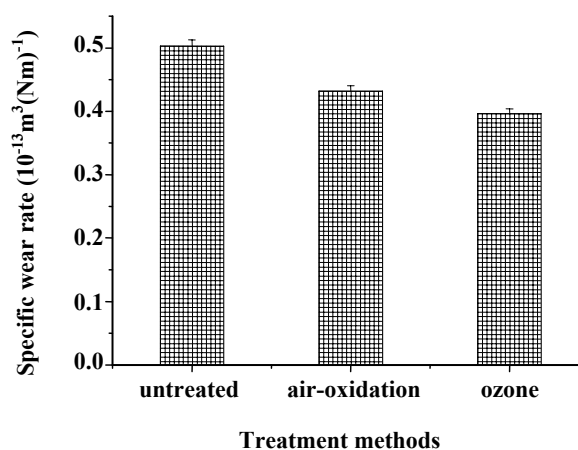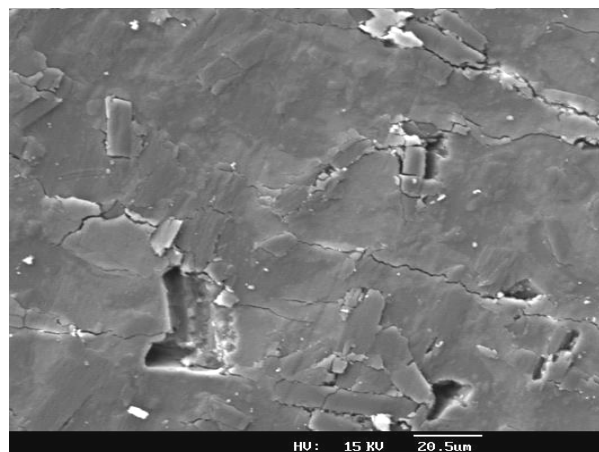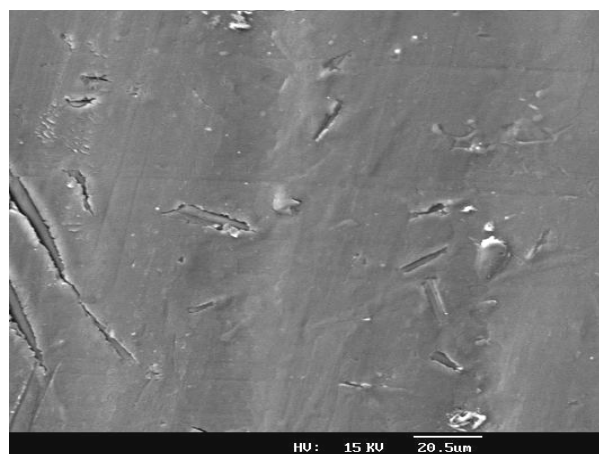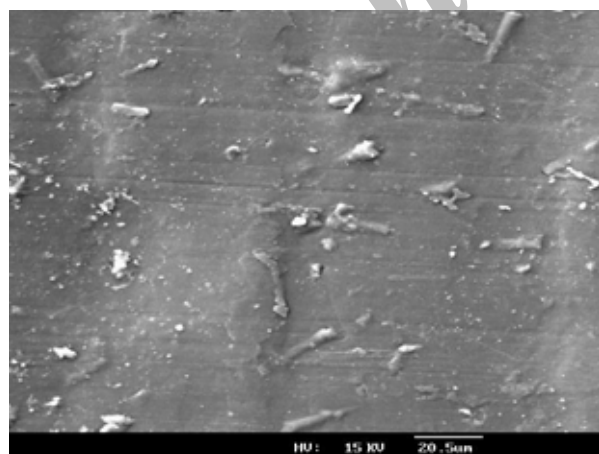

Fig. 5: Specific wear rate of PA6 composites under a load of 12 N and a reciprocating sliding frequency of 8 Hz.

(a)untreated

(b)air oxidation

(c)ozone

Fig. 6: SEM photographs of the worn surfaces of PA6 composites.

as shown in fig 6(a). Deep pores exist between carbon fibers and PA6 matrix, which indicates that there is a very poor interfacial adhesion between the fiber and the PA6 matrix. So the untreated fibers are more prone to be peeled off due to the weak interface bonding. The fillers are easily detached from the matrix under a load of 12 N leaving cavities whose boundaries are the same shape as the filler fibers remove. Many cavities within the matrix material structure lead to many 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 more susceptible to fracture. Therefore, the load-carrying capability of the composite is reduced resulting in a decrease in wear resistance property.

On the worn surfaces of the PA6 composites containing the modified fibers, the damage became weaker, indicating the effective action of the surface modification of carbon fibers upon the improvement of the wear resistance of the PA6 composites, as shown in Fig. 6(b) and (c). For the air-oxidized CF/PA6 composite, the worn surface is smoother than the untreated one, as seen in Fig. 6(b). There are also pores between carbon fibers and PA6. This indicates that the interfacial adhesion between carbon fibers and PA6 is not strong enough, even though carbon fibers are air-oxidized. Poor interaction leads to high abrasion wear due to the ease of fiber cracking or pull-out. The reinforcing fibers 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 fiber-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 fiber/matrix interface and passes between the fibers 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 fibers bare. The driving force for the crack comes from the friction forces being applied on the matrix surface. Where the fibers are close to each other the matrix between the fibers are often fragmented and broken off when the

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Table 1: The O1s/C1s ratios and elemental composition.

Surface treatment	Elementary composition / %			Atom ratio / %	
	C	O	N	O/C	N/C
Untreated	82.38	8.27	9.35	10.05	11.34
Air oxidation	77.75	13.15	8.34	16.91	10.73
ozone	51.1	17.6	31.3	34.45	61.01

Table 2: Relative percentage of functional groups on surface treated carbon fibers.

	Relative atomic percentage of functional groups		
	C=C (284.6 eV)	C—O (286.1-286.3 eV)	O—C =O (288.8-289.1 eV)
untreated	95.8	2.9	1.3
ozone treatment	63.28	17.58	19.13

crack propagates along the fiber surface. Additionally, the cavity shown in the PA6 matrix is the result of a filler carbon fiber 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 fibers, as shown in fig 6(c), the worn surface is quite smooth and no cracks are visible. CF and PA6 are compactly bonded and no pores exist between the fiber and the matrix. This indicates that the filler carbon fibers in ozone treated CF/PA6 have good bonding to the matrix and support the load from the counter body effectively. The carbon fibers are not easy to be detached from the PA6 matrix in friction process due to the improvement of the interfacial adhesion between the carbon fibers and PA6 matrix after ozone treatment. Thus, the load is effectively supported by carbon fibers and the large-scale transfer and rubbed-off of PA6 will be restrained. Accordingly, the wear of the PA6 composite filled with ozone treated carbon fibers was reduced.

The O1s/C1s ratios and elemental composition changes caused by surface modification on the surface of carbon fibers are shown in Table1. The above ratio for the modified fibers is increased compared to unmodified fibers. The untreated fibers display the smallest O1s/C1s ratio (10.05%) and ozone treated samples show high O1s/C1s ratios (34.45%). Ozone treatment enlarges this amount significantly and it decreases the concentration of C1s.

To study the changes of carbon surfaces, the specific ratio of each oxygen functional group in the C1s regime is showed in Table 2. It was found that the oxygen

functional groups including the C—O (BE=286.1-286.3eV) and O—C=O (BE=288.8-289.1 eV) were increased after treatment, but the C=C group decreased. This result means that surface treatment probably breaks the C=C (BE=284.6 eV) bond and binds oxygen functional groups on the fiber surfaces.

The C1s peaks are deconvoluted into surface functional group contributions of the samples and shown in Fig. 7. It is found that the C1s peak of the ozone treated carbon fiber can be fitted to three line shapes with binding energies at 284.6, 286.1 and 288.9 eV assigned to graphitic C=C bond, C–O and O–C=O [14].

It is well known that the surface functional groups, especially oxygen-containing groups, of carbon fibers play an important role in improving the surface-free energy and adhesion between the fiber and matrix [15]. XPS studies show that ozone treatment increases the amount of carboxyl groups on carbon fiber surface, which is helpful to increase the interfacial adhesion between carbon fiber and PA6.

CONCLUSIONS

In this study, we investigated the effect of ozone treatment on interfacial and tribological properties of carbon fiber-reinforced PA6 composites. As a result, the IFSS of the composites were improved by ozone treatment. Ozone treatment effectively promotes the interfacial adhesion between the carbon fiber and PA6 matrix. IFSS values of the composites with ozone treated carbon fiber are increased by 60% compared to that without treatment. XPS results show that ozone treatment
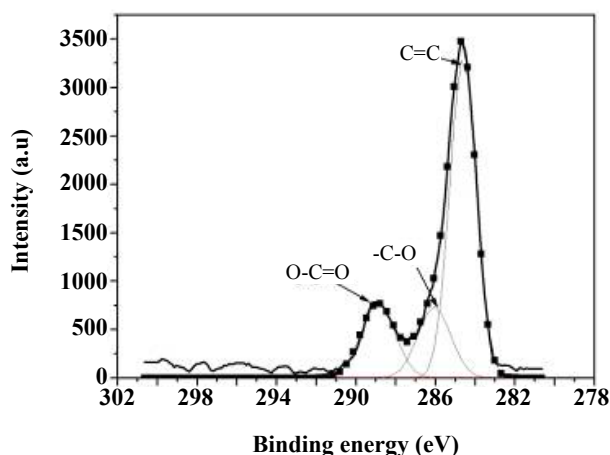
Fig. 7: Curve fit of C1s photoelectron peak of ozone treated CF.

increases the amount of carboxyl groups on carbon fiber surface, thus the interfacial adhesion between carbon fiber and PA6 matrix is effectively promoted.

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