************ ∛材料、机械工程 ∦

Influence of carbonization on structural and mechanical properties of PAN/phenolic-based carbon/carbon composites

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Abstract: Poly-acrylonitrile (PAN)/phenolic-based carbon/carbon (C/C) composites manufactured by the wet layup method are potential materials for the application of high-performance structures. In order to understand the influence of carbonization step on structural and mechanical properties of PAN/phenolic-based carbon/carbon composites, the interlaminar fracture toughness (mode II) is tested. The correlation of formation mechanisms of crack with structural characteristics is important for preparation of C/C-SiC composites. The structural characteristics of the composites are characterized by Archimedes's method, scanning electron microscopy (SEM) and three-point bend tests. Experimental results show that the interlaminar fracture toughness of carbon/carbon specimens is 59. 7% of that of the carbon fiber reinforced phenolic resin-based plastics (CFRP) specimens.

Key words: PAN/phenolic-based carbon/carbon composites; carbonization; three-point bend test; fracture toughness

0 Introduction

Poly-acrylonitrile (PAN)/phenolic-based carbon/carbon (C/C) composites have been considered as the most promising material for space/aviation industries and general structural applications due to dimensional stability, invariability of material property, high strength and rigidity, as well as corrosion resistance^[1-4]. The versatile properties of phenolic-based carbon justify their applications as matrices in different kinds of composites^[1,3]. Some of the most important advantages are the modest price, the wide spectrum of obtainable properties and the high carbon yields. The carbon yields allow the conversion of carbon fiber reinforced phenolic resin-based plastics (CFRP) to high temperature composites, such as C/C, C/C-SiC and C/C-Cu composites^[5-7]. The performances of PAN/ phenolic-based carbon/carbon composites are known to depend on the types of carbon fibers, matrix precursors, nature of bonding between the fiber and the matrix, and processing conditions^[8-14]. Schulte-Fischedick, *et al*^[15]

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clarified the stress state during the pyrolysis at temperature above 500 °C. Due to the shrinkage of the matrix and the hindering of stiff carbon fibers, the matrix experienced a tensile stress and the tensile stress applied to the matrix increased with the rising of pyrolysis temperature. When the tensile stress locally exceeded the tensile strength of the matrix, the first cracks appeared at the weakest sites, such as the fiber/matrix interface, pores or cracks^[16-19].

In order to understand the mechanical properties of PAN/phenolic-based carbon/ carbon composites, several studies have been carried out^[16,18-22]. But on the other hand, very limited information available is on the study of interlaminar fracture toughness (mode II) of these composites. Therefore, this paper studies the effect of carbonization on structural and mechanical properties of PAN/phenolic-based carbon/carbon composites. The interlaminar fracture toughness was determined by experiments. The numerical analyses were conducted by using interlaminar fracture toughness data obtained from the experiments. These numerical analyses were then used to interpret the variations in mechanical properties.

1 Experimentation

1.1 Materials

The reinforcements for carbon/carbon composites, 3K PAN-based high strength fibers (supplied by Toray Industries Inc., Japan) were chosen. For the matrix materials, phenolic resins adopted in this study were FB resins (supplied by Bengbu High-Temperature Resin Factory, China). Resistant The characteristics of the as-received materials are listed in Tab. 1.

Tab. 1 Characteristics of carbon fiber and FB resin

Materials	Appearance	Composition	$Density/(g \cdot cm^{-3})$	Tensile strength/MPa	Tensile modulus/GPa	Diameter/µm
Carbon fiber	Black	w(C)≥93%	1.76	3 530	230	7
FB resin	Yellow	w(C)≥69%	1.28	≥71	≥3.6	3-20

1.2 Preparation of CFRP and C/C composites

CFRP composites manufactured by wet layup method is shown in Fig. 1. A composite was made by using 20 layers of the carbon fiber fabrics $(0^{\circ}/90^{\circ})$ of thickness 4.0 to 4.5 mm. The carbon fiber fabrics were placed into an open metallic moulds with an inner dimension of 100 $mm \times 70 mm \times 60 mm$, and wet out with the phenolic resin using a consolidation roller. The fiber volume fraction was set to about 50% (nominal) in the CFRP composites. Before producing moulding compounds, the inner walls of metallic mould were coated with a siliconreleasing agent and dried at room temperature for 30 min. The produced moulding compounds were cured at 150 °C for 10 h. After cooling down to room temperature, the CFRP specimens were removed from the metallic moulds, and the specimens were then machined. The CFRP composites were also post-cured at 240 °C in ambient atmosphere for 8 h, and then pyrolyzed to convert into C/C composites. Pyrolysis (carbonization step) of the CFRP composites was performed at the temperature of $1\ 000\ ^{\circ}C$ for 1 h at the rate of 10 $^{\circ}C/min$ in a nitrogen atmosphere. Schematic diagram of the fabrication method and the image for CFRP and C/C composites are shown in Fig. 2.



Fig. 1 Schematic diagram of wet layup method

1.3 Measurement

The analytical balance with an accuracy of 0.1 mg was used to measure the mass variation of the specimens before and after pyrolysis. The determinations of density (ρ_s) and porosity (V_v) of the specimens using Archimedes principle



Fig. 2 Schematic diagram of the fabrication method, and the images for CFRP and C/C composites

were carried out in accordance with ASTM D792. The density and porosity are given by Eqs. (1) and (2), respectively:

$$\rho_{\rm s} = m\rho_0/(m_1 - m_2) \tag{1}$$

$$V_{\rm v} = 100 - \rho_{\rm s} \left(\frac{w_{\rm matrix}}{\rho_{\rm matrix}} + \frac{w_{\rm fiber}}{\rho_{\rm fiber}} \right) \tag{2}$$

where w_{matrix} is the mass fraction of matrix, w_{fiber} is the mass fraction of fiber, ρ_{matrix} is the density of matrix, ρ_{fiber} is the density of fiber, ρ_0 is the density of water, m is the specimen mass in the air, m_1 is the specimen mass measured after being immersed in the water for 24 h and then wiped, and m_2 is the specimen mass in distilled water.

Interlaminar fracture toughnesses of the specimens from CFRP and C/C specimens were analyzed using the three-point bend test^[20-22]. These specimens were cut of the size 60 mm×10 mm×(4, 0-4, 5) mm. Straight notches from each specimens of 0.15 mm width were prepared using an Isomet machine. In this paper, the ratio of notch depth (a) to length (S_0) of specimens 1 : 4, span length 40 mm and a crosshead speed 0. 5 mm/min were kept. Bending load was applied perpendicular to the specimens. The specimen geometry was used to determine the mode II delamination fracture toughness^[20].

2 Results and discussion

2.1 Morphological properties

The density and porosity measurements (Tab. 2) show whether a specimen is fully dense, and can be expected to stand up in infiltration process^[17,23-24]. During the pyrolysis (carbonization step), the evolution of gaseous products resulted in chemical densification,

formation of pores and cracks and the rearrangement of structures. The porosity of the composites largely increased, while in the carbonization process the density of the composites gradually decreased.

Tab. 2The void volume fraction and the actual
density values of composites

Specimen	m/g	m_1/g	m_2/g	$ ho_{\rm s}/({ m g}\cdot{ m cm}^{-3})$	$V_{ m v}$ / $\%$
CFRP	166.8	208.6	95	1.47	3.95
C/C	162.8	210.6	85	1.29	17.70

Fig. 3 shows the large cracks and the development of angle cracks which run at an angle with the longitudinal fiber bundle. In this study, observation in SEM image, density and porosity measurements indicate that the C/C composites have more cracks, lower density and higher porosity than CFRP composites.



Fig. 3 SEM micrograph of C/C composites derived from the PAN/phenolic resins composites with carbonization up to 1 000 ℃

2.2 Interlaminar fracture toughness (Mode II)

Load-displacement curves were obtained during the tests and the front location of crack was marked on the CFRP and C/C composites specimens during crack propagation. In order to eliminate the effect of a relatively blunt artificial crack, the initial crack propagation step was ignored and the crack length was adjusted correspondingly to the location of nascent crack tip. The critical energy release rate in Mode II, $G_{\rm IIc}$, of the specimens can be approximated with the following Eqs. (3), (4) and (5):

$$G_{\rm IIc} = 9a^2 P^2 C/2b(2L^3 + 3a^3) \tag{3}$$

$$C = (3a^3 + L^3)/2bh^3 E_1$$
 (4)

$$E_1 I = P L^3 / 48\delta \tag{5}$$

where P is the critical load for crack initiation, C is the compliance, a is the crack length (between the support point and the edge of the crack), L

is the support span, δ is the displacement, I is the moment of inertia of area, b and h are the width of the specimen and half thickness respectively, and E_1 is the longitudinal modulus.

From Fig. 4 (a), interlaminar fracture toughness shows the trend of increase as the deflection velocity of load point increases, and significantly higher interlaminar fracture toughness of CFRP specimen compared to C/C specimen. The peak values give the maximum load, which is required for the crack to propagate through the specimens. It is indicated that the fiber volume fraction in the composite controls its toughness. However, some variation was expected due to the void content level. From the Fig. 4(b), crack surfaces slide with friction, and thus dissipate part of the external work in the form of mode II. Load-displacement traces were used in the calculation of the final $G_{\rm Hc}$, the values of CFRP and C/C are 421.3 and 251.5 kJ/m² separately.



Fig. 4 Load vs. displacement curves for CFRP and C/C specimens, and mode II loads for a C/C specimen during fracture testing

3 Conclusions

The PAN/phenolic-based carbon/carbon composites were prepared by pyrolyzing the carbon fiber reinforced phenolic resin-based plastics. The density of the C/C composites is 1. 29 g/cm³ and the porosity is 17. 70%. Changes in structural characteristics happen as phenolic resin/carbon fiber composites are converted to a carbon/carbon fiber composites after carbonization at 1 000 °C in N₂. Bulk density decreases and the porosity increases progressively after pyrolysis at 1 000 °C. The developing of the cracks mainly depended on the reaction velocity and pyrolysis mechanism of the resin at 1 000 °C. It is found that interlaminar fracture toughness of the C/C composites is 59.7% of that of the CFRP composites. The major outcome of the above investigations has established the fact that the porous carbon preforms potential structural material candidate for new processing technologies with a wide range of technological applications, especially as C/C-SiC and C/C-Cu composites.

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炭化对聚丙烯腈/酚醛基炭/炭复合材料结构和力学性能影响

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摘要:由湿法叠涂制得的聚丙烯腈(PAN)/酚醛基碳/碳(C/C)复合材料在高性能结构材料领域具有应用潜力.为了了解炭化步骤对聚丙烯腈/酚醛基碳/碳复合材料结构和力学性能的影响,进行了层间断裂韧性(模式 II)测试.由于结构特征与裂纹形成机理的相互关系对 C/C-SiC 复合材料的制备很重要,采用阿基米德方法、扫描电子显微镜(SEM)和三点弯曲试验对复合材料的结构进行表征.实验结果显示,碳/碳(C/C)试件的层间断裂韧性为碳纤维增强酚醛塑料(CFRP)试件的 59.7%.

关键词:聚丙烯腈/酚醛基炭/炭复合材料;炭化;三点弯曲试验;断裂韧性 中图分类号:TB330.1 文献标识码:A doi:10.7511/dllgxb201503005

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