CHARACTERIZATION OF FIBER/MATRIX BONDING STRENTH DURING THE PYROLYSIS OF CFRP TO C/C COMPOSITES

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1 Introduction

Because of their excellent thermo-mechanical properties and high temperature microstructural stabilities, carbon fiber reinforced ceramic matrix composites (CMCs) are considered to be promising materials for the application of high-performance structures [1-3], such as advanced tribological systems, thermal protection systems and propulsion systems. One of the most interesting CMCs is the C/C-SiC composite via liquid silicon infiltration (LSI) process [1,3].

The manufacturing of C/C-SiC composites via the LSI process can be divided into three steps: (i) fabrication of a carbon fiber reinforced plastic (CFRP) green body from C fibers and thermosetting resin; (ii) carbonization of CFRP green body by pyrolysis of resin matrix above 900 ºC to obtain the C/C preform; (iii) siliconization of carbon in carbon/carbon preform via the infiltration of liquid silicon at temperatures above its melting point of 1420 ºC.

At the carbonization step, the micro-crack pattern developed during the pyrolysis of resin plays a key role on the infiltration of liquid silicon. The cracks act as the communication channels for the liquid silicon climbing into the C/C preform and allow the conversion of Si and C to SiC during the infiltration process. The crack pattern and crack density formed during the carbonization step have a strong influence on the mechanical durability and the microstructure integrity of C/C-SiC composites.

In the literature [3], authors have found that the fiber/matrix bonding strength is a very important factor which governs the formation of the micro-crack pattern during pyrolysis. In order to know the microstructure evolution mechanism during pyrolysis of CFRP, therefore, it is quite necessary to clarity the evolution of interfacial bonding strength between fiber and matrix during the pyrolysis of CFRP to C/C preform.

The single fiber push-out by micro-indentation test is a suitable method which allows the in situ characterization of interfaces in realistic multi-fiber composites. Several researchers have tried to apply the same indentation methods to the same materials. However, none of them succeeded in obtaining clearly defined interfacial strength. Because carbon fibers possess lower compressive strength and smaller diameter than SiC fiber, the maximum load applied to a carbon fiber was extremely small. Furthermore, the specimen thickness had to be thinner than 100 um. However, one-time resin infiltrated C/C composite is very weak and brittle. To prepare C/C thin specimen is quite difficult.

In the present work, an ultra-low load micro-indentation tester was applied to characterize the fiber/matrix bonding strength in order to understand the forming mechanism of micro-crack pattern during the pyrolysis of CFRP to C/C composite.

2 Experimental

PAN-based carbon fibers and phenolic resin were used to fabricate the CFRP green body by resin transfer moulding (RTM) route. The prepared CFRP was post-cured at 200 °C in ambient atmosphere. To establish the temperatures of interest, firstly a thermographometric (TG) analysis was performed on CFRP as shown in Fig. 1. The TG-curve provides data when change in the morphology could occur. After analyzing the TG-curve, some samples were subjected to 300 °C, 400 °C, 500 °C, 600 °C, 900 °C

and 1500 °C pyrolysis and subsequently tested in the fiber push-out.

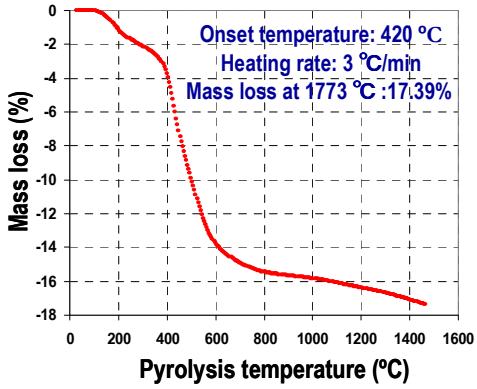

Fig. 1. Thermo-gravimetric data for the pyrolysis of CFRP to C/C composite.

Fig. 2 schematically illustrates the preparation and setting of the specimen for the single fiber push-out test. A groove was cut into the polished surface of the specimen holder in order to make room for the pushed-out fiber. The load was applied on the single fiber's end above the groove. To obtain the thin specimen, the specimen were polished on both sides with a thickness smaller than 100 um. Due to the pyrolized CFRP above 500 °C is very weak, in order to avoid the damage of pyrolized CFRP during the polishing, the cured CFRP specimen with high toughness and pyrolized CFRP were stuck on the specimen holder together for protecting the pyrolized CFRP. And also, the polishing should be proceeded slowly and the force applied to the slices was minimized. To ensure a quality finish, diamond slurry with gradually reduced particle size from 9 to 1um was used.

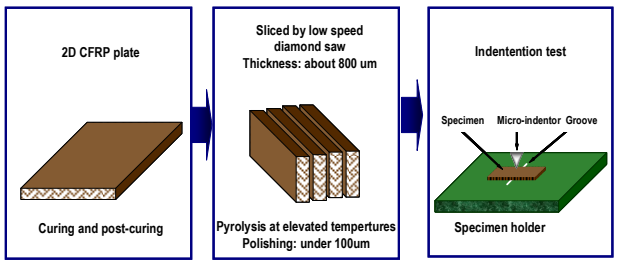

Fig. 2. Schematic illustration of specimen preparation for single fiber push-out test.

Single fiber push-out tests were conducted by an ultra-low load micro-indentation tester (FisherScope H100: maximum loaded capacity of 1000 mN, load resolution: ± 0.02 mN, displacement resolution: ± 2 nm). A square-based indenter tip with an apex angle of 136º was used for the loading introduction. After the testes, the pushed-out fibers were confirmed by the observation of Scanning Electronic Microscopy (SEM). The maximum load for indentation test was optimized based on the value of thickness of the specimen and load-displacement curves. In the present study, the interfacial shear strength, τ_b, in the push-out tests was calculated by the Eq. (1) according to the load obtained from the flat region of the load-displacement curve as shown in Fig. 3 of latter section:

$$\tau_b = \frac{P}{2\pi r_f L} \qquad (1)$$

where P is the load applied to a fiber's end after a complete interface debonding, r_f is the fiber radius, and L is the specimen thickness. For each specimen, a statistical valid number of about 60 fiber push-out tests were performed. The average interfacial shear strength was analyzed by using the two-parameter Weibull statistical theory [4].

3 Result and discussion

Fig. 3 shows the typical curves of fiber/matrix interface shear stress (ISS) vs. indentation displacement of single fiber push-out tests for CFRP pyrolized at different temperatures. It is clear that the curves of successfully tested specimen were similar in shape.

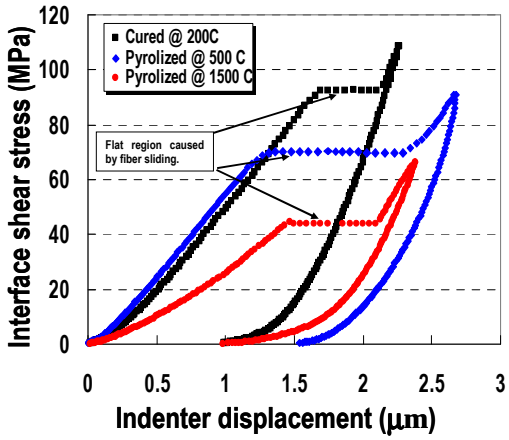

Fig. 3. Typical shear stress vs. indentation displacement curve of single fiber push-out tests for the CFRP after treatment at different

temperatures.

From Fig. 3, it can be seen that a non-linearity is observed at the preliminary stages of loading curves, which is caused by a combination of elastic deformation of the fiber and matrix as well as the situation of indented area. With increasing indentation displacement, the slope of the curve decreased, indicating crack initiation and a stable propagation at the interface of fiber and matrix. As the stress increases to a certain value the shear stress stays constant as the displacement increases leading to an occurrence of flat region as shown in Fig. 3.

It should be noted that the specimen should be thin enough to allow fractures over the whole interface of the loaded fiber and to ensure complete fibre push-out. If the specimen is too thick, there is no flat region occurred during the fiber push-out test.

The flat region indicates the occurrence of complete de-bonding of the fiber/matrix interface accompanied by a sliding of fiber. The level of flat region varied with the pyrolysis temperatures. With increasing the pyrolysis temperature, the level of flat region clearly decreased. Due to the pyrolized specimen shows a porous structure, to ensure the successful test and reduce the data scattering, the indentation test for pyrolized specimen should select the fiber with good matrix surrounding.

The displacement in the stress-displacement curve of the composite was confirmed by the observation of pushed-out fibres in SEM as shown in Fig. 4.

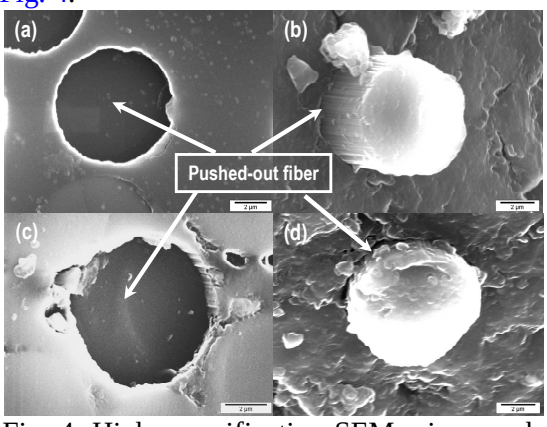

Fig. 4. High magnification SEM micrographs: (a) the top micrograph of pushed-out fibers and (b) the bottom micrograph of pushed-out fibers for CFRP cured at 200 ºC; (c) the top micrograph of pushed-out fibers and (d) the bottom micrograph of pushed-out fibers for CFRP pyrolized at 900 ºC.

The interfacial shear strength τ_b was determined by the stress of the flat region. Fig. 4 clearly shows the complete fiber/matrix de-bonding which corresponds to the occurrence of flat region in Fig. 3. No fiber fracture and matrix cracking was observed in the micrograph even for the specimen pyrolized at 1500 ºC as shown in Fig. 4 (c) and (d). The images clearly show the indented fiber is lower on the push-in top surface. Additionally, the other end of the pushed-out fiber protrudes from the bottom surface of the matrix.

Fig. 5 shows the changing ISS of composites as a function of the pyrolysis temperature. The scattering is probably the result of a non-homogeneity of the morphologies of interface between fiber and matrix such as a variation of density and distribution of defects (pores, bubbles and cracks) during curing and pyrolysis. Micro-pores distributed in the matrix close to the interface of fiber/matrix have been reported in literature [5].

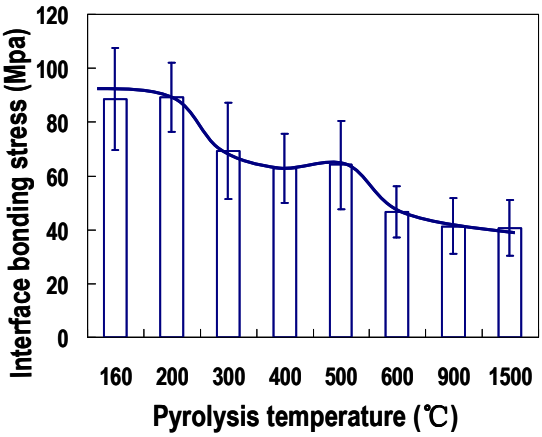

Fig. 5. Interfacial shear stress as a function of pyrolysis temperature.

The CFRP cured at 160 ºC shows maximum ISS, which decreases during pyrolysis at elevated temperatures. The ISS determined for composites in the C/C state is similar to values reported in literature [6]. The decreased ISS as increasing the pyrolysis temperature could be attributed to the generation of volatiles and resin matrix degradation [7]. From the TG data shown in Fig. 1, we can conclude that the main pyrolysis of the resin matrix starts at about 400 ºC. During the main pyrolysis phase (between 400 °C and 600 °C), a significant gas generation degrades the matrix structure, leading

to decreased ISS. At temperatures above 600 ºC, the resin matrix is carbonized into amorphous carbon. The interfacial shear strength degrades towards a low value with a relatively small scattering as shown in Fig. 5. The low ISS for the pyrolized specimen can be attributed to weak chemical bonding and the defect effect. Because the C/C-preform contains many voids, process cracks and partial interfacial de-bonding, these defects probably act as a source of fractures during loading. When the single fiber push-out tests are conducted, the defects that are present in the stressed area tend to become larger.

A slight increase of ISS at about 500ºC was observed as shown in Fig. 5. This increase might be attributed to the physical changes and chemical reactions within the matrix [8-9]. During pyrolysis above 400 ºC, the structure of the phenolic resin is transformed gradually into a glassy and isotropic carbon structure [8-9]. In comparison to the converting matrix, the carbon fiber has a very low coefficient of thermal expansion along the fiber axis [5]. During heating at 500 ºC, the resin matrix is subjected to significant thermal expansion, but the low CTE of the fiber bundle in 0º direction restrains the thermal expansion of resin matrix within 90º fiber bundles. This thermal expansion effect is irreversible during cooling, and causes an additional clamping force to fibers, resulting in an increased ISS. Raman study of microstructure changes of phenolic resin during pyrolysis shows a new peak appearing at 500°C, while the original peak completely disappeared above 600°C [10]. The newly formed peak is caused by the formation of glassy carbon structures. Such chemical reactions also have a contribution to the increased ISS. The result obtained in the present work would be useful in understanding the microstructure evolution mechanism during the pyrolysis of CFRP to C/C composites. Furthermore, this data can be applied to the modeling work for the analysis of fiber/matrix interface failure and distribution of transverse cracks [11].

4 Summary

The fiber/matrix bonding strength during the pyrolysis of CFRP to C/C composite was measured by single fiber push-out test with a micro-indentation method. The composites in their polymeric state show a high fiber/matrix bonding strength. After pyrolysis at elevated temperatures the fiber/matrix bonding strength decreases. Such result would be beneficial to the understanding of microstructure evolution mechanism during the pyrolysis of CFRP to C/C composites.

Acknowledgments

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