Materials Science & Engineering A 685 (2017) 65–70

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

# A reconsideration of the relationship between structural features and mechanical properties of carbon fibers

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ARTICLE INFO

*Keywords:*
Carbon fiber
Microvoid
Shear compliance
Tensile strength
Stress relaxation
Surface fractal

ABSTRACT

The relationship between mechanical properties and micro-structures of carbon fibers was reconsidered based on the "elastic unwrinkling" model and Griffith microcracks theory. Experimental results showed, stress relaxation and elastic unwrinkling process could both be observed in non-graphitic fibers, the tensile deformation of which was suitable to be described by "elastic unwrinkling" model. However, elastic unwrinkling process was not so obvious in graphitic fibers since the recrystallization of the crystalline structure had changed the shear compliance of the carbon lattice. A correction towards the compliance was proposed in this case based on the surface fractal of the graphitic fibers. On the other hand, the relationship between tensile strength and the void's parameter of carbon fibers was found generally follow the Griffith equation. In addition, some factors besides of voids, e.g., the local density fluctuation etc., were also found indirectly related to the tensile fracture process of carbon fibers, while a complete exposition of the influencing mechanism remained to be further explored.

## 1. Introduction

A growing body of literature suggests that the mechanical properties are mainly determined by the structural defects within the carbon body or the surface of carbon fibers [1,2]. The structure features of these defects existing in the forms of microvoid and surface flaw etc. were suggested having direct relationship with the control precision of the technologies during the production of the fibers [1–4]. Nowadays, series of high-performance carbon fibers realize industrialization and become important reinforcement materials, along with the great improvement of the involved technologies and their control precision. A widespread theory for these fibers is that they universally share a common point-the refinement in structure as well as the stability in properties. In this case, large pore and surface flaw can no longer be detected simply by intuitionistic means such as SEM etc [5]. This might mean, the high quality of the manufacturing techniques and process control technologies have reduced or even largely eliminated these large scale defects, while the elimination of large scale defects has further improve the performance of the resulting fibers [5]. Then what is the main factor or constraint in this case for the properties of these fibers without large scale defects?

The performance of the commercially available carbon fibers showed fibers with high strength usually have a large elongation at break. As shown in Table 1, these fibers have a relatively low tensile modulus because of the large elongation. On the other hand, high modulus fibers tend to have a small elongation at break, due to which their modulus is relatively higher. In this work, the performance of these two types of fibers was found relevant to their microstructure (e.g., microcrystalline, microvoid and their preferred orientation) and the resulting fracture mechanism. The statistical result based on Table 1 can also be interpreted in the scope of variety of the microstructure of carbon fibers.

## 2. Experimental

### 2.1. Samples

Carbon fibers of different sources including commercially available fibers (T300B and T700SC of Toray Co., Japan), homemade fibers (HNCF and TGCF) and their graphitized samples (the 1800 °C-, 2000 °C-, 2300 °C- and 2500 °C-treated graphitic fibers of T300B which were respectively noted as T3-1800, T3-1800, T3-2000, T3-2300 and T3-2500, and 2800 °C-treated graphitic fibers of HNCF and TGCF which were respectively noted as HNGF and TGGF) were used in the experiment. The sizing agent on the fiber surface was removed by Soxhlet extractor with 2-Butanone as the solvent before the experi-

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http://dx.doi.org/10.1016/j.msea.2017.01.006
Received 29 July 2016; Received in revised form 31 December 2016; Accepted 2 January 2017
Available online 03 January 2017
0921-5093/ 

**Table 1**
The properties of carbon fibers from Toray Industries, Inc [2].

| Series | Tensile strength ( GPa ) | Tensile modulus ( GPa ) | Elongation at break ( % ) |
|---|---|---|---|
| T300B | 3.53 | 230 | 1.5 |
| T700SC | 4.90 | 230 | 2.1 |
| T800H | 5.49 | 294 | 1.9 |
| T1000SC | 5.88 | 294 | 2.2 |
| M40JB | 4.41 | 377 | 1.2 |
| M55JB | 4.02 | 540 | 0.8 |
| M60JB | 3.92 | 588 | 0.7 |

ment.

### 2.2. Characterization

Crystallite parameters of the samples were investigated by using an X-ray diffractometer (PANalytical X'Pert PRO, CuKa, λ=0.1541 nm, 40 kV, 40 mA) with a fiber specimen attachment. Measurements were made by performing equatorial scan, meridianal scan, as well as azimuthal scan at the fixed Bragg position. The diffraction curves were fitted by MDI Jade 5.0 and the structural parameters were obtained according to Bragg equation and Scherrer formula [6]. The Raman experiment was performed on Raman spectrometer (LabRam HR Evolution and XPLORA, Jobin-Yvon). The structural parameters were obtained through a Lorentz fitting to the data [7,8]. The SAXS experiment was performed for all the samples on a long-slit collimating SAXSess mc2 instrument ($\lambda_{CuKa}$=0.15418 nm, Anton Paar GmbH) operated at 40 kV, 50 mA in vacuum. Approximately 1 mm thick bundles of fibers were arranged parallel on the sample holder to conduct the experiment. The scattered X-ray intensity was recorded using an image plate detector, and each measurement was recorded for an hour. The desmearing of collimating error and the background correction of SAXS data were done by SAXS-quant 1.01 software included with the instrument. The relevant data and methodology can be referenced in our previous works [5,9,10]. The tensile test was performed on the AG-1 universal material tester (Shimadzu Co., Ltd., Japan) based on GB/T3362-2005 “Test methods for tensile properties of carbon fiber multifilament”. The fracture samples were also collected for the cross-section morphology observation using field emission scanning electron microscope (SEM: JSM-6320F, JEOL). The bulk Density was measured by flotation method based on ISO 10119:2002 “Carbon fiber-Determination of density”.

## 3. The fracture mechanism of carbon fibers

### 3.1. The influence of internal stress on tensile modulus

It was reported in previous works, Raman G band (~1580 $cm^{-1}$) of carbon fibers showed red shift with the increase of heat treatment temperature during the graphitization [10]. As shown in Fig. 1(a), the red shift phenomenon was found having some influence on the tensile modulus. Kobayashi et al. held that red shift represent the change of the residual stress/strain within the carbon rings, and is a kind of internal stress relaxation induced by the external force or thermal effect [11]. It seems when external tensile force was applied to the fiber, internal tensile strain start in those turbostratic structures in order to withstand the force [10,12]. In microscopic scale, the twisted condition of those turbostratic layers in this case will be eased by the induced microstrain, and sequentially release the residual stress therein [7,12–15].

As shown in Fig. 1(b), results from X-ray diffraction, on the other hand, indicated that 100/101 reflection shift to the lower angle area with the increase of tensile modulus [10]. This phenomenon should be another evidence for the influence of internal stress on tensile modulus, because the $d_{10}$ spacing calculated directly based on 100 reflection is also a sensitive parameter related to internal stress within the carbon rings [10,11,16]. However, we cannot go further to assert the internal stress as a conclusive factor for tensile modulus, because the former is not independent parameter but has some connection with another important structure feature, i.e. the preferred orientation of carbon planes. In previous works, we found the wrinkled turbostratic layers with a poor orientation and larger $d_{10}$ than that of graphite are essentially a representation for the underlying residual stress [5,10]. In other words, the influence of stress can be brought into the orientation effect and integrated as a single question, i.e. the relationship between tensile modulus and the preferred orientation of carbon planes.

### 3.2. Tensile fracture mechanism of different types of carbon fibers

A growing body of literature suggests that the structure heterogeneity have an effect on the mechanical property of carbon fibers, and will realize the influence through changing the tensile fracture behavior [9,17]. As shown in Fig. 2, the fracture surface of as-received T300B fiber is of great roughness, and the fracture source (indicated by the red arrow) as well as the extending process of cracks can be clearly detected. The stress concentration zone which will turn into the fracture source during the tensile fracture was estimated to be located in the fiber surface. However, for graphitized fibers the tensile fracture mode has changed greatly, and the fracture source is no longer detectable by SEM etc. The fracture seems to have started from the whole skin region and transferred inward to the core, as speculated based on the fracture morphology. We believe the heterogeneous distribution of the internal stress plays an important role in the incipient fracture of the skin [10]. As was reported, the compressive stress within the carbon crystallites of the skin was released more sufficient than that of the core region during the graphitization of carbon fibers [10]. In this case, the strain usually can not extend in the skin as easily as that in the core when external stress was applied, i.e. the skin might overload first when the applied stress cannot be sufficiently transferred to the core of the fiber. Then the fracture will start near the skin and transferred to the core, after which a tensile failure of the fiber happens.

All in all, the high-modulus graphitic fibers are different from high-strength fibers in fracture mechanism, and a remarkable hint for this is that they have varying levels of elongation at break. Two extreme cases will help us in understanding their differences during the tensile fracture. As shown in Fig. 3, the high-strength carbon fibers are generally composed of two-dimension turbostratic crystallites poorly oriented along the fiber axis, which implies the existence of plentiful internal stress. During the tensile test, the fiber will thus experience at least four stages, i.e. the external stress application, the internal stress release, the crack initiation and propagation, and finally fracture failure in order of time. It is worth noting that, induced by the applied stress the wrinkled turbostratic layers will unwrinkle and the orientation of the crystallites will thus be enhanced along with the release of internal compressive stress. That is why the crystalline structure was observed to be improved and the preferred orientation strengthened during the tensile experiment [12,18]. A rough fracture surface, an obvious fracture source as well as its propagation path are generally the main features for the tensile fracture of high-strength fiber.

The main difference between high-modulus graphitic fiber and high-strength carbon fiber according to our observation is that the former tends to have an inconspicuous stress release process (i.e. the elastic unwrinkling process of the turbostratic layers) during the tensile experiment. As was reported, the compressive stress within the carbon crystallites was released more sufficient in high-modulus graphitic fibers than that in high-strength non-graphitic fibers, and as well more sufficient in the skin than that in the core for almost all the fibers [5,9,10]. The carbon layers within the crystalline structure of these