

The Effect of Nanostructure upon the Mechanical Properties of Carbon Fibres

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論文内容要約

Polyacrylonitrile (PAN)-based carbon fibres were first developed in 1959 and now play an important role in the production of lightweight structural materials. Their world annual production is greater than 70,000 tonnes, and the PAN-based carbon fibre market has been growing at ~10% per annum. Furthermore, considerable opportunities exist for tailoring their properties and the internal structure to suit performance requirements. To optimize and improve the properties of carbon fibres, the factors which control their mechanical properties, such as Young's modulus, tensile strength and compressive strength, must be understood. Studies of graphite and rayon-based carbon fibres which were first graphitized were undertaken, followed by studies of high-performance types of PAN-based carbon fibres which contain large proportions of amorphous carbon. Although the amorphous structures in the carbon fibres have not been clarified because of the difficulty in analysing them, numerous researchers have recognized the importance of amorphous phases. Therefore, we developed an approach to elucidate the behaviour of amorphous carbon by dividing carbon fibres into two clearly different components and then calculating the differential behaviour between the composite and crystalline components of the fibres. The conclusions of this thesis are as follows:

Chapter 2 discusses the structures of both crystalline and amorphous carbon to address the relationship between these phases in the subsequent chapter on the basis of the structure. We investigated the sp^3 structure in PAN- and pitch-based carbon fibres by UV-Raman spectroscopy. We found, on the basis of the intensity ratios of the T-, D- and G-bands, that the proportion of sp^3 carbon in PAN-based carbon fibres with Young's moduli in the range from 200 to ~300 GPa is approximately 10–25%, whereas that in PAN-based carbon fibres with Young's moduli greater than 350 GPa is ~5%. In contrast, pitch-based fibres were found to contain very little sp^3 carbon, which can be correlated with their relatively low shear moduli and poor compressive strength.

Chapter 3 discusses the effect of the nanostructure of carbon fibres on their deformation micromechanics. We introduced the Mori-Tanaka theory as a new micromechanical model to predict Young's modulus of carbon fibres; this model considers both the crystalline and amorphous components of the carbon fibre structure, shown in Figure 1. The axial elastic constants of

the bulk carbon fibres were directly measured by X-ray diffraction (XRD), and an axial shear modulus of approximately 20 GPa was calculated (Table 1). The elastic constants of amorphous carbon in the fibres and the volume fractions of crystallites were estimated by micromechanical models. We found that the amorphous modulus was approximately 0.2 TPa and that the volume fractions of crystallites were 0.4–0.8, depending on the nanostructure of the carbon fibres. Also, because the Raman G-band shift rate per unit strain is known to be related to the crystallite modulus, the data indicated a nearly constant value of 1.0 TPa, which is consistent with the results of direct measurements of graphene. The results clearly show that the behaviour of carbon fibres can be expressed by a composite mechanical model which assumes that they consist of both crystalline and amorphous carbon components.

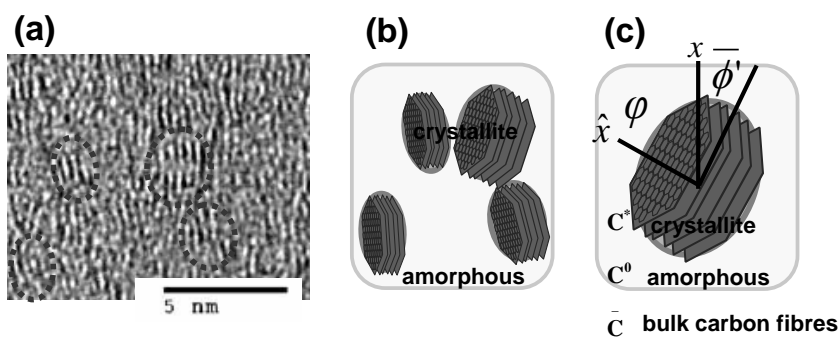


Figure 1. (a) a High resolution TEM image of the T800G fibre and schematic of (b) the structure and (c) the modeling of (b), where φ is the orientation angle, \hat{x} is the layer axis of the carbon layer stacks and x is the fibre axis.

Table 1. Physical and mechanical properties of the bulk carbon fibres and their components; the crystalline and amorphous phase.

Fibre	Bulk carbon fibres					Components of fibres	
	Young's modulus /GPa	L_c /nm	$\langle \cos^2 \varphi \rangle$	Axial elastic constants /GPa	Axial shear modulus /GPa	Amorphous modulus /GPa	Crystallinity
1000°C	220	1.6	0.067	333	24.9	159	0.458
T800G	255	2.0	0.064	434	27.1	200	0.508
M30S	261	2.4	0.057	454	22.0	186	0.551
M40S	360	3.8	0.042	579	18.4	211	0.633
M50S	440	5.8	0.026	739	11.2	212	0.770

Chapter 4 details our study of the fracture mechanism of different modulus types of carbon fibres, where the stress distribution within single fibres, flaw size and fracture toughness are considered. Single-fibre strength was precisely measured by fragmentation tests of single-fibre composites. Fracture probability was constant with respect to strength in the range from 2 to ~4 GPa; in contrast, it increased with the fibre modulus when the strength was greater than or equal to 4 GPa. The fracture toughness of the carbon fibres, which we obtained by introducing notches with lengths in the range from 60 to ~200 nm, was approximately $1.1 \text{ MPa m}^{1/2}$. It was suggested that the fracture toughness of the carbon fibres may be strongly limited by the nanostructure of the amorphous carbon in the fibres due to the linear relationship between the fracture toughness and the amorphous modulus (Figure 2). Although the average flaw size in the low/intermediate-modulus-type carbon fibres was 50 nm for a gauge length of 10 mm, the average flaw size was larger for the high-modulus-type fibres. These results suggested that the crack growth of surface flaws on a scale of tens of nanometres occurred during carbonization treatment.

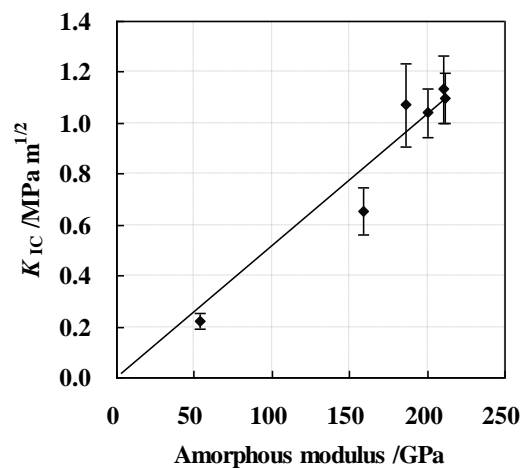


Figure 2. The relationship between the fracture toughness of the carbon fibres and the Young's modulus of the amorphous carbon within the fibres.

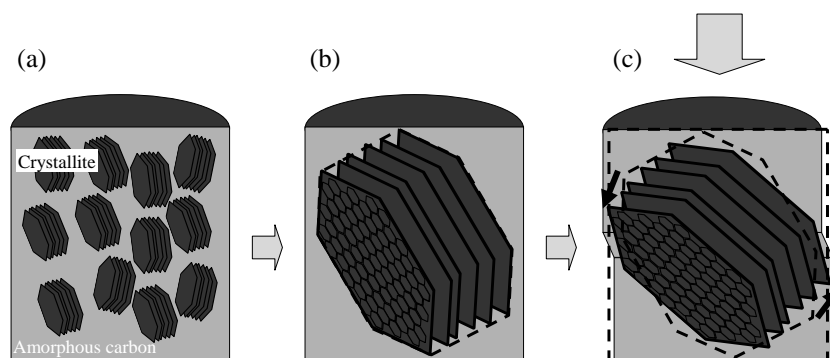


Figure 3. Modelling of fibre structure. (a) the model consisting of crystalline and amorphous structure, simplified model of (b) before compression and (c) after compression.

In Chapter 5, we address the relationship between the structure and compressive strength of carbon fibres in detail. To determine compressive strength, we employed a combination of single-fibre composite tests and Raman spectroscopy. We found that the compressive stress–strain curves showed non-linear behaviour with modulus softening under compression. The compressive strength of the fibres with a modulus ≥ 400 GPa was measured to be ≤ 2 GPa, and that for the fibres with a modulus < 400 GPa were > 2 GPa. We introduced a model to explain this behaviour, which assumes that the fibres behave as composites consisting of both crystalline and amorphous components. Compressive strength is suggested to be controlled by the critical stress for kinking the crystallites in the fibres (Figure 3). Hence, the compressive strength of carbon fibres was found to depend on the shear modulus of the fibres and the orientation of the crystallites within them.

This study has important implications for understanding the structural parameters, such as the amorphous modulus and crystallinity, which control the Young's modulus of PAN-based carbon fibres. Carbon fibres have impressive mechanical properties, which can be controlled at the nanoscale by the mixture of sp^2 and sp^3 carbon components. We believe that this study provides a processing method which allows certain mechanical properties, such as Young's modulus, to be further improved. Hence, considerable opportunities exist for improving the mechanical properties of carbon fibres, i.e. Young's modulus, tensile strength and compressive strength, using the knowledge gained in this study. The results of this investigation will contribute to the prevention of global warming (by reducing CO_2 levels) by the adoption of novel materials which we expect to develop in the future.