Nanostructure in Carbon Fibres and Its Effect upon Tensile Failure

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論文内容要約

Today, polyacrylonitrile (PAN)-based carbon fibres are playing an important role in various industrial fields due to their excellent mechanical performances combined with lightness. Global demand for PAN-based carbon fibre is believed to be in steady increase at least until 2030s. There are however still challenges for PAN-based carbon fibres to be adopted in wider field such as automotive application. The most important challenge that prevents carbon fibres to be adopted drastically in such application fields would be relatively higher cost of current carbon fibres as compared to that of conventional materials such as steels, aluminium alloy. We believe that more efficient design for carbon fibres, such that the mechanical performances are maximised with reducing the production cost at the same time, is possible through closer understanding of their structure-properties relation. In our series of previous studies, we have discussed the effect of nanostructures upon stiffness, tensile strength and compressive strength of carbon fibres, by introducing micromechanics based analysis. In these studies, it was suggested that carbon fibres are a sort of composite materials that consist of crystallites and amorphous (disordered) part. We have understood that this disordered part plays a striking role in determining mechanical properties. In order to improve mechanical properties of the disordered part within carbon fibres, closer understanding upon its nanostructure is necessary. In addition, in order to set a reasonable target for improving mechanical properties of carbon fibres a knowledge upon maximum reachable strength is important.

In chapter 1, the history and the current state-of-art for the carbon fibres are reviewed so as to clarify the aim of this study. First, the material characteristics of carbon fibres and their fields of application are described, followed by the introduction to the typical manufacturing steps in case of PAN-based carbon fibres. Second part of this chapter describes the history of carbon fibres as well as its market developments. In particular, emphasis was placed upon the relation between market growth and the scale up of the carbon fibre manufacturing. Third part then discusses the progresses in understanding the structure and its effect upon the mechanical properties of carbon fibres. Through these sections the current status of carbon fibres are reviewed, which finally leads to the aim of the present study.

In chapter 2, a novel experimental technique is developed in order to assess the tensile strength at gauge length significantly shorter than that of the conventional tensile test. The loop test, which was first utilised by Jones to measure the so-called "intrinsic strength" of carbon fibres, was known to be suitable for evaluating the tensile strength at short gauge length. Although there has so far been several reports regarding the characterisation of carbon fibres using the loop test, none of them commented on the validity of the stress estimation in the loop test of carbon fibres, which show strong nonlinear elasticity and premature failure in compressive side. To address this drawback, we combined the loop test with the Raman stress measurements based upon the stress-dependant band shift. The accuracy of the stress evaluation at the loop top by this novel technique is discussed in comparison to the conventional estimation based upon the elastica theory. With this technique the single fibre tensile strengths at the gauge length of a few tens of μm was quantitatively evaluated for the first time. It was found that the tensile strength as high as 13 GPa was observed for the commercially-available Torayca® T800S carbon fibre, suggesting its considerable potential in terms of the further improvements in the tensile strength. From a fractographic as well as a statistical analysis, it was suggested that the tensile strength at this length scale is affected by the nanostructures within PAN-based carbon fibres.

In chapter 3, the tensile failure phenomena in carbon fibres is investigated by means of the novel technique developed in chapter 2. A series of PAN-based carbon fibres, which have different Young's moduli, is investigated using this technique. A micromechanics based analysis suggested that the tensile failure at the extremely short gauge length, or the intrinsic strength, is initiated at the disordered part rather than at the crystallites contrarily to what have been suggested in literature. In specific, the intrinsic strength was found to be reasonably explained by the tensile failure of the disordered part near the pole of the crystallites, which act as stress concentrators (Table 1). This understanding prompted us to further investigate the nanostructure, especially the disordered part, of carbon fibres.

Table 1. Aspect ratio of the crystallites r,(=L_a/L_c), stress concentration factor α and estimated inherent tensile strength of the disordered region σ_d.

	Aspect ratio r (=L_a/L_c)	SCF α (for k=1)	Inherent tensile strength of the disordered region σ_d /GPa (for k=1)	Young's moduli for the disordered region E_d /GPa
CF1	0.9	1.5	4.1	43
CF2	1.3	1.7	16.9	159
T800S	1.4	1.7	19.5	200
CF3	1.5	1.8	18.7	193
CF4	1.9	2.0	18.5	211
CF5	2.1	2.1	18.9	212

In chapter 4, in order to obtain insights into the disordered part in carbon fibres, the nanostructures in PAN-based carbon fibre is investigated using Raman spectroscopy. Since there has been difficulties in relating the Raman spectra for PAN-based carbon fibres to its corresponding nanostructures, due mainly to its broad spectral shape, we focus on its excitation wavelengths (energies) dependent change in the spectral line shape. Observed Raman spectra using Deep-UV excitation showed no T band, suggesting that PAN-based carbon fibres consist predominantly of the sp^2 hybridised carbon. Furthermore, in contrast to the graphitic carbon that shows no D band in the UV excitation, several PAN-based carbon fibres showed the residual D band even in the UV excitation, showing that PAN-based carbon fibres contain the graphitic and the disordered part (Figure 1). In order to separate out the contributions of each nanostructural component from the observed Raman spectra for carbon fibres, an analytical equation that combines the so-called Tuinstra-Koenig relation and the rule-of-mixture was introduced. The excitation energy dependence of the disordered part estimated using this analytical model suggested that the disordered part in PAN-based carbon fibres are made of the sp^2 carbon clusters. In addition to this, it was suggested that the sp^2 carbon layers undergo significant development at the expense of the sp^2 carbon clusters during carbonisation heat treatment, resulting in the complete loss of the sp^2 carbon clusters for high modulus PAN-based carbon fibres (Figure 2). We understood that this lateral growth of the sp^2 carbon layers plays a key role, through a highly crosslinked sp^2 carbon network, in determining the excellent mechanical performances of PAN-based carbon fibres.

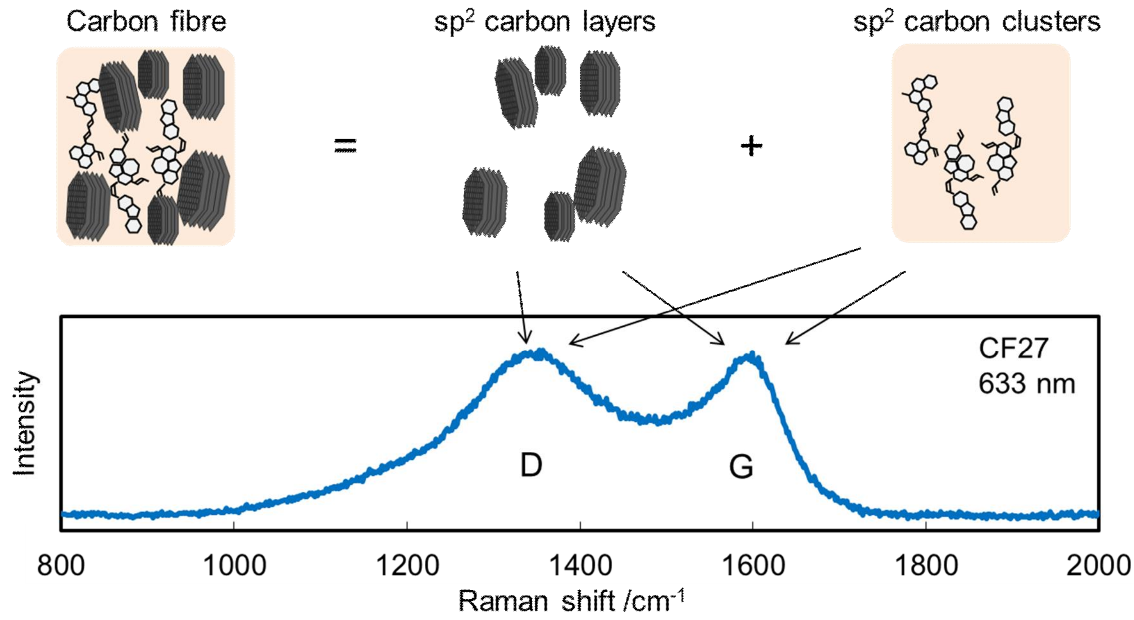

Figure 1. Peak assignments of the Raman spectra based on the plausible nanostructure of PAN-based carbon fibres.

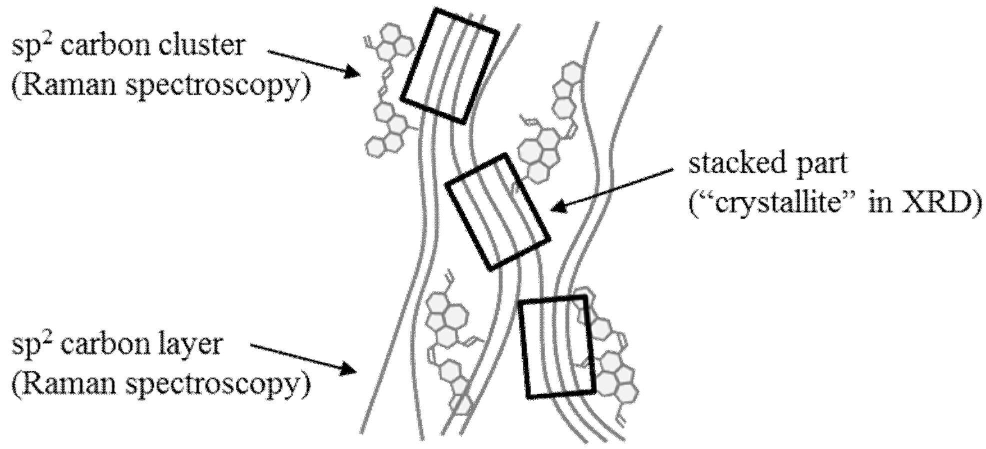

Figure 2. The depiction of the nanostructures in PAN-based carbon fibres.