



Investigating nanostructures in carbon fibres using Raman spectroscopy



Haruki Okuda^{a, b, d, *}, Robert J. Young^b, Daniel Wolverson^c, Fumihiko Tanaka^a, Go Yamamoto^d, Tomonaga Okabe^d

^a Composite Materials Research Laboratories, TORAY Industries, Inc., 1515 Tsutsui, Masaki-cho, Iyo-gun, Ehime, 791-3193, Japan

^b School of Materials, University of Manchester, Grosvenor Street, Manchester, M1 7HS, UK

^c Department of Physics, University of Bath, Claverton Down, Bath, BA2 7AY, UK

^d Department of Aerospace Engineering, Tohoku University, 6-6-01, Aoba-yama, Aoba-ku, Sendai, Miyagi, 980-8579, Japan

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ABSTRACT

Nanostructures in the PAN-based carbon fibres were investigated by means of the Raman spectroscopy which was performed using a series of different excitation wavelengths. UV-Raman measurements showed the predominance of sp^2 carbon for the carbon fibres with Young's moduli ranging from 55 to 440 GPa. The excitation wavelength dependence of the spectral line shape implied the presence of the graphitic (sp^2 carbon layers) as well as the amorphous carbon-like component (sp^2 carbon clusters) in these fibres. An analytical model based upon the Tuinstra-Koenig relation and the rule-of-mixtures concept was proposed to account for the observed behaviour of the peak intensity ratio I_D/I_G . It was suggested that the carbonisation heat treatment led to the sp^2 carbon layers extending rapidly throughout the nanostructure, resulting in the complete loss of the sp^2 carbon clusters for the higher-modulus carbon fibres. These new findings together with the proposed analytical model are believed to be essential keys towards the development of new generation carbon fibres.

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1. Introduction

Due to their excellent mechanical performance per weight, polyacrylonitrile (PAN)-based carbon fibres have widely been accepted in a broad range of industrial applications [1]. Throughout the development history of the PAN-based carbon fibres, understanding their structure-property relation has always been one of the central subjects in order to further improve their capabilities. We have recently demonstrated that the mechanical properties of the PAN-based carbon fibres, such as tensile modulus [2], tensile strength [3,4] and compressive strength [5] can be reasonably explained by assuming carbon fibres being nanocomposites which consist of the crystallites and a disordered part [6–8]. It is therefore thought that clear insights into the detailed structure of these components, in particular the disordered part, is essential for further improving the performance of the PAN-based carbon fibres.

There have already been a number of studies regarding the

nanostructure of the carbon fibres based upon a variety of techniques which includes wide-angle X-ray diffraction (WAXD) [9,10], small-angle X-ray scattering (SAXS) [10–13], transmission electron microscope (TEM), selected-area electron diffraction (SAED) [14–16] and Raman spectroscopy [17–20]. As compared to the crystallites, however, the understanding upon the disordered part in the carbon fibres is limited, possibly due to the lack of suitable analytical techniques. Recently, Raman spectroscopy has been applied extensively to a broad range of carbon materials from graphitic [23–25] to amorphous carbon materials [26–29] as a powerful tool to characterise their nanostructure, since each different carbon material shows its own spectral line shape in their Raman spectra. In addition to this, the spectral line shape of the carbon materials changes drastically depending upon the excitation wavelengths and this dependence can be used as a unique fingerprint for identifying the type of carbon materials [23–28]. It is thus expected that both the crystallites and the disordered part in the carbon fibres could be characterised in details by means of the Raman spectroscopy using multiple laser wavelengths. To the best of our knowledge, however, there has been no such report in which Raman spectra have been used to investigate the detailed structure

* Corresponding author. Composite Materials Research Laboratories, TORAY Industries, Inc., 1515 Tsutsui, Masaki-cho, Iyo-gun, Ehime, 791-3193, Japan.

E-mail address: Haruki.Okuda@nts.toray.co.jp (H. Okuda).

of the each component in the carbon fibres. One of the main reasons for this, we believe, is the lack of an appropriate framework that enables the separation of the contributions from the individual components in the Raman spectra of carbon fibres.

In order to quantitatively analyse the Raman spectra for the carbon fibres, a curve fitting method which is universally applicable to a wide range of carbon fibres is necessary. Various curve fitting methods have proposed in literature so far for the analysis of the Raman spectra of the carbon fibres. Melanitis and coworkers fitted the D, G and D' bands of the Raman spectra for some intermediate- and high-modulus carbon fibres using a set of three Lorentzian functions [17]. Frank applied two Lorentzian functions in order to fit the G band [18]. Vautard et al. introduced three Lorentzian functions in order to fit the D, G band and a shoulder around 1100 cm^{-1} , respectively [21]. Zickler et al. used five Voigt functions to fit the Raman spectra for a variety of PAN- as well as pitch-based carbon fibres [22]. In these conventional fitting approaches, the broad spectral line shape of the carbon fibres often requires an additional peak between the D and G bands [22]. For the amorphous carbon materials, this residual intensity adjacent to the G band has been explained as the asymmetric tail of the G band. Several researchers have pointed out that the Breit-Wigner-Fano (BWF) function successfully reproduces the asymmetric G band of sp^2 carbon materials [26,29]. Considering that the carbon fibres are made up of crystallites and a disordered part, it is expected that the BWF function is also applicable to the curve fitting of the Raman spectra for the carbon fibres.

In this study, the nanostructures of the carbon fibres were investigated by means of the Raman spectroscopy using a series of different excitation wavelengths with an aim of clarifying the key for further improvements the mechanical performance of the PAN-based carbon fibres.

2. Experimental

2.1. Materials

PAN-based carbon fibres that are thought to represent a wide range of different nanostructures were used in this study (Table 1). No surface treatment was applied for these fibre samples after carbonisation or graphitisation to avoid any possible spurious effects due to the changes in the surface structure. Density was determined on the basis of the buoyancy method using *o*-dichloroethylene. Prior to the experiments, fibre samples were washed with acetone at room temperature, followed by the air-drying, to remove any impurities. For the Raman measurements, a small number of fibres were attached on a slide glass with

Table 1

The physical and the mechanical properties of the carbon fibres studied. The crystallite sizes L_c , L_a , which denote the average thickness of the crystallites, the average diameter of the crystallites parallel to the fibre axis, respectively, and the orientation parameter π_{002} were evaluated using WAXD [10].

	Young's Modulus /GPa	Density / gcm^{-3}	Diameter / μm	L_c /nm	L_a /nm	π_{002} /-
CF13	55	1.57	6.6	1.3	1.3	0.815
CF15	150	1.78	6.2	1.3	1.5	0.815
CF17	200	1.82	6.0	1.3	1.7	0.819
CF19	240	1.78	5.8	1.4	1.9	0.822
CF21	272	1.80	5.7	1.4	2.1	0.823
CF24	294	1.80	5.5	1.3	2.4	0.825
CF27	294	1.80	5.5	1.9	2.7	0.821
CF36	294	1.73	5.6	2.4	3.6	0.845
CF72	380	1.80	5.4	3.7	7.2	0.883
CF100	440	1.85	5.3	4.7	10.0	0.904

adhesive tape. In order to avoid possible artefact peaks from the slide glass, these fibres were attached with one end being located 5 mm away from an edge of the slide glass as depicted in Fig. 1. These fibre samples were confirmed to show no skin-core differences in their Raman spectra as shown in the supplementary information.

2.2. Methods

All the WAXD measurements were performed at the beam line BL03XU/Spring-8 (Frontier Softmaterial Beamline "FSBL") of the Japanese Synchrotron Radiation Facility. The incident beam of the wavelength of 0.08 nm was used to irradiate bundles of about 300 individual fibres. The diffracted beam was captured with a flat panel detector which was positioned at a distance of about 5–10 cm from the fibre bundle. The fibre axis was set perpendicular to the incident beam for the measurement of the 002 reflection, while the angle between the fibre axis and the incident beam was adjusted by about $10\text{--}15^\circ$ for evaluating the 10 reflection. Measurements were repeated twice and the 2D diffraction patterns thus obtained were averaged. The reflection peak profiles against the 2θ direction were obtained by integrating the 2D reflection patterns with a small azimuthal angle of $\pm 30^\circ$ and 5° for the 002 and the 10 peaks, respectively. The average thickness L_c and the average diameter of the crystallites parallel to the fibre axis L_a were evaluated from the peak profiles of the 002 and the 10 reflections, respectively, according to the method of Shioya et al. [10]. The orientation parameter π_{002} was calculated from the azimuthal profile of the 002 reflection [10].

Raman spectra for the excitation wavelengths of 830 nm (1.49 eV, IR), 633 nm (1.96 eV) and 514 nm (2.41 eV) were measured using a Renishaw 1000 spectrometer. For 488 nm (2.54 eV) and 325 nm (3.82 eV, UV), a Horiba-Jobin-Yvon LabRam was used. Measurements using 244 nm (5.08 eV, deep-UV) were performed using Renishaw 2000 spectrometer. In order to avoid any effect associated with heating, the laser power at fibre surface was adjusted to be less than 3 mW using ND filters. Magnification of the objective lens was $50\times$, giving a beam spot diameter of around $2\mu\text{m}$ [30], throughout the study except for the UV (325 nm) and deep-UV (244 nm) excitation, for which the objective magnification employed was $40\times$. The incident laser beam was linearly polarised with the polarisation direction always being parallel to the fibre axis. No analyser was used in this study. All the measurements were performed three times and averaged.

In this study, Raman spectra were analysed using a combination of fitting functions which contain a Voigt function, two Gaussian functions and an asymmetric Lorentzian function. Specifically, a Voigt function, Gaussian function and asymmetric Lorentzian function were selected with intention to fit the D, D' and G band, respectively. The remaining Gaussian function was used to account for a shoulder peak at around 1100 cm^{-1} . This package of fitting functions is designed to be applicable to the Raman spectra for a

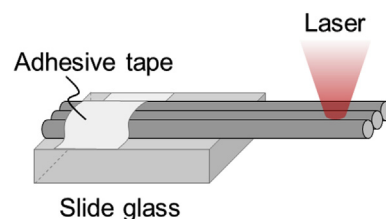


Fig. 1. Geometry of the Raman measurements. (A colour version of this figure can be viewed online.)

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