Mechanical anisotropy of PAN-based and pitch-based carbon fibers

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Abstract
With the expansion of use of carbon fiber reinforced plastics (CFRPs), it becomes important to obtain precise knowledge of elastic properties carbon fibers in radial direction as well as axial direction. Although the elastic property in radial direction of polyacrylonitrile (PAN)-based carbon fibers have been investigated using ultrasound scatter measurements, compression tests of single fibers and nanoindentation, there is no experimental evaluation for the pitch-based carbon fibers which possess higher crystallinity and tensile modulus than PAN-based carbon fibers. Here, we investigate the mechanical anisotropy of PAN- and pitch-based carbon fibers by the nanoindentation technique. Nanoindentation tests are carried out on longitudinal (0°), 45° and transversal (90°) cross sections of carbon fibers by a Hysitron TriboScope (Minneapolis, MN) using a diamond conical indenter with a nominal tip radius of 10 μm. We demonstrate that the indentation modulus of both carbon fibers decreases with a decreasing orientation angle from axial to radial direction, but this tendency is more significant in the pitch-based carbon fibers. Supposing that the indentation modulus in the radial direction is same as the transverse elastic modulus, the anisotropy of elastic modulus \( E_f/E_T \) of the pitch-based carbon fibers is calculated to be 165 which is approximately 15 times as high as that of PAN-based carbon fiber \( (E_f/E_T = 11) \). This result suggests that the pitch-based carbon fiber possesses a large mechanical anisotropy. The higher mechanical anisotropy observed in the pitch-based carbon fiber is mainly due to the existence of the parallel arrangement carbon crystallite microtexture with high crystallinity in the axial direction.

Keywords: Carbon fibers, Nanoindentation, Indentation modulus, Anisotropy

1. Introduction

As carbon fibers have high specific strength and specific modulus, they are widely used as reinforcements in composite materials. Depending on the precursors or the subsequent processing conditions employed, the microstructures and mechanical properties of carbon fibers significantly vary over a wide range. Carbon fibers are normally classified as PAN- or pitch-based, depending on the precursor source, being either polyacrylonitrile (PAN) or meso-pitch respectively. The microstructures and elastic properties in the axial direction of carbon fibers are well characterized by an X-ray diffraction (XRD) technique, Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and mechanical (tensile and flexural) tests (Vezie, et al., 1990; Huang and Young, 1995; Tanaka, et al., 2013; Northolt, et al., 1991; Naito, et al., 2009; Newcomb, 2016). On the other hand, there are some studies examining the transverse elastic modulus (i.e. an elastic property in the radial direction) and mechanical anisotropy (Maurin, et al., 2008; Csanádi, et al., 2017; Naito, et al., 2017; Tane, et al., 2019). However, in the above previous studies, PAN-based carbon fibers have been widely used and there is a current lack of knowledge in the literature regarding mechanical properties of pitch-based carbon fibers which possess a significantly different...
microstructure and mechanical properties (630–940 GPa in tensile modulus) compared with the PAN-based carbon fibers whose tensile moduli are 230–290 GPa for high-strength PAN-based fibers and 350–560 GPa for high-modulus PAN-based fibers (Naito, et al., 2008, 2017). For a comprehensive understanding of mechanical anisotropy of carbon fibers, the evaluation of micro- and nanostructures and transverse elastic property of pitch-based carbon fibers are needed.

In this study, nanoindentation of pitch-based carbon fibers is performed on three different cross sections to assess the anisotropic characteristics of the mechanical properties of carbon fibers. Indentation techniques are an excellent method to measure mechanical properties on small regions. Especially, micro- and nanoindentation tests are widely applied in materials with small size. They have been used to study mechanical behaviors of carbon fibers (Maurin, et al., 2008; Sun, et al., 2014; Csanádi, et al., 2017) as well as metals (Gouldstone, et al., 2000) and ceramics (Page, et al., 1992). We also systematically investigated the crystallinity and nanostructure of carbon fibers by means of SEM, TEM and Raman spectroscopy. For comparison, structural and mechanical properties of a PAN-based carbon fiber were also evaluated.

2. Experimental procedure

Carbon fibers used in the study included high modulus pitch-based (K13D) carbon fibers as well as high strength PAN-based (T700SC) carbon fibers. PAN-based and pitch-based carbon fibers were supplied by Toray Industries, Inc and Mitsubishi Chemical Corporation, respectively. The diameter and density for PAN- and pitch-based carbon fibers are 7.05 ± 0.56 μm and 11.72 ± 0.36 μm in diameter and 1.8 g/cm³ and 2.2 g/cm³ in density, respectively. The cross-sectional microstructures of the single carbon fibers, which were obtained from tensile testing (with a gauge length of 25 mm), were observed by SEM (FEI Quanta 200FEG, USA). The nanostructures of carbon fibers were examined using a TEM (Hitachi H-9000NAR) at an operating voltage of 200 kV, and nanobeam electron diffraction (NBD) technique was performed along the fiber axis. To prepare the TEM sample, the carbon fibers were molded in a room-temperature curing epoxy resin, followed by cutting to a relatively thin section (<100 nm) using a focused ion beam (FIB, FEI, Strata DB235 M, USA). Raman scattering spectroscopy (JASCO, NRS-7100, Japan) was used to evaluate the crystallinity of single carbon fibers. A green laser with an excitation wavelength of 532 nm was irradiated perpendicularly to the surface of single carbon fibers which were placed on a piece of paper. The measurements were conducted at room temperature under ambient conditions. The laser power was 2.5–2.8 mW and the exposure time was 20 s.

Carbon fiber reinforced plastic (CFRP) prepreg sheets were cut into the appropriate size and fiber orientation, and CFRP laminates were made using hand layup and vacuum bagging technique (no bleeder). The prepreg sheets containing T700SC carbon fibers and K13D carbon fibers were cured in 120°C for 4 h followed by 135°C for 2 h and 180°C for 4 h, respectively at the pressure of 0.5 MPa by an autoclave (Ashida Mfg. Co., Ltd., ACA Series) in the laboratory. The laminate configurations were [0/+45/90/-45]₁₄ for the T700SC CFRP and [0/+45/90/-45]₁₂₀ for the K13D CFRP, respectively. The fiber volume fractions of the composites containing T700SC and K13D were 53.9 and 54.5 vol.%, respectively. The nominal thickness of the composites was approximately 14 mm. The CFRP laminates were cut with dimensions of 10 × 10 × 14 mm³. To produce cross sections of carbon fibers for nanoindentation testing, the CFRP samples were embedded in epoxy resin then polished.

To evaluate the mechanical anisotropy of single carbon fibers, nanoindentation tests were carried out on longitudinal (0°), 45° and transversal (90°) cross sections of carbon fibers where the indentation direction is assumed to be perpendicular (radial direction), 45° and parallel to the fiber axis, respectively. Selected surface areas covering these orientations were tested by a Hysitron TriboScope (Minneapolis, MN) using a diamond conical indenter with a nominal tip radius of 10 μm. On each orientation, more than 30 indents were prepared, and the loading time and the unloading time were 20 s with 5 s holding time. A maximum indentation depth is selected as 140 nm and 110 nm for the PAN- and pitch-based carbon fiber, respectively, to control the contact depth in the range from 80 nm to 100 nm. The indentation modulus was automatically calculated according to the standards of instrumented indentation (Oliver-Pharr method (Oliver and Pharr, 2004)). The indenter tip was calibrated prior to the measurement on a quartz which resulted in an accurate tip area function. Young’s modulus and Poisson’s ratio of the diamond tip were Eᵣ = 1140 GPa and νᵣ = 0.07, respectively. The shape of fibers assumed to be transversal (90°) and 45° cross section were analyzed by scanning probe microscope (SPM) images and the tilt angle of fibers (α) was calculated by α = cos⁻¹(r/R), where r and R are the
minor and major radii of carbon fibers. On the transversal (90°) cross section, the indentation modulus and tilt angle of 60 fibers were measured, and the carbon fibers within the tilt angle of 10° were used to calculate the average indentation modulus in the axial direction.

3. Results and discussion

SEM and TEM images of the carbon fibers are shown in Fig. 1. The structure of carbon fibers varies with the synthesis method. The PAN-based carbon fiber exhibits rough, rather poorly defined granular texture. The Raman intensity ratio \( (I_G/I_D) \) shown in Fig. 2(a) is measured to be approximately 1. Extant studies reported similar rough texture for similar and other PAN-based carbon fibers (Vezie, et al., 1990; Kumar, et al., 1993; Kulkarni and Ochoa, 2006). However, the pitch-based carbon fiber derived from an anisotropic pitch exhibits a sheet-like texture. Its crystallinity is higher than those of PAN-based carbon fibers and its Raman intensity ratio is approximately 10 as shown in Fig. 2(b). A similar sheet-like texture was reported for similar and other high modulus pitch-based single carbon fibers (Huang and Young, 1994; Paiva, et al., 2000).

Fig. 1 SEM micrographs of cross-sectional views for (a1) PAN-based (T700SC) and (b1) pitch-based (K13D) single carbon fibers. TEM images of transversal cross-sectional views for (a2) T700SC and (b2) K13D carbon fibers and longitudinal views for (a3) T700SC and (b3) K13D carbon fibers. Insets shown in (a3) and (b3) give NBD patterns of carbon fibers. The PAN-based carbon fiber possesses rough, rather poorly defined granular texture, whilst the pitch-based carbon fiber derived exhibits a sheet-like texture.

Fig. 2 Raman spectra of (a) PAN-based (T700SC) and (b) pitch-based (K13D) carbon fibers. The spectral positions of both the D-band and G-band were calibrated using an emission spectrum of known wavenumber (1712 cm\(^{-1}\)) from a Ne lamp. The relative intensity ratio of the G-band to D-band peak, i.e., \( R = I_G/I_D \), of the T700SC and K13D carbon fibers are approximately 1 and 10.
Scanning probe microscope (SPM) images of two types of carbon fibers with different orientation are shown in Fig. 3. Nanoindentation was performed on transversal (90°), 45° and longitudinal (0°) cross sections of carbon fibers. After the tests, the residual imprints are not discernible suggesting that the deformation of carbon fibers is mostly elastic. This observation is confirmed by the characteristic load-displacement curves indicated in Fig. 4, which suggests elastic deformation of carbon fibers. Fig. 4 shows also that the transversal cross section of the PAN- and pitch-based carbon fibers requires about four and ten times as high a load as the longitudinal one to generate the same penetration depth. The orientation dependence of indentation modulus is shown in Fig. 5, where the average indentation modulus of the PAN-based carbon fiber for axial, 45° and radial direction is 73.4 ± 5.5 GPa, 28.3 ± 1.6 GPa and 20.9 ± 2.0 GPa, respectively. These values are in agreement with a recent nanoindentation report on PAN-based carbon fibers (Csanádi, et al. 2017). On the other hand, the pitch-based carbon fiber in the axial direction exhibits a similar indentation modulus (76.5 ± 11.6 GPa) in comparison to the PAN-based carbon fiber for the same orientation, whilst the indentation moduli of the pitch-based carbon fiber in the 45° and radial direction are smaller than those of PAN-based carbon fiber (13.3 ± 2.1 GPa and 5.7 ± 1.4 GPa). The indentation modulus decreases with a decreasing orientation angle from axial to radial direction. The reduction of the indentation modulus is significant for low orientation angle (from axial to 45° direction), and its tendency is more remarkable for the pitch-based carbon fiber (83% reduction) compared with the PAN-based carbon fiber (62% reduction). From 45° to radial direction, the indentation modulus decreases moderately, but its reduction rate is more significant for the pitch-based carbon fiber (26% and 57% decreases for PAN- and pitch-based fibers).

To date, Raman spectroscopy and TEM observation have been used successfully in the structural characterization of carbon fibers (Huang and Young, 1995; Naito, et al., 2017). As shown in Fig. 1, the random microtexture with folded or crumpled sheets can be observed in the cross section of PAN-based carbon fibers by TEM. With respect to the longitudinal views of TEM images, the composition of PAN-based carbon fibers is assumed to consist of at least two phases such as entangled and crumpled carbon sheets (crystallite phase) and amorphous carbon. These features correspond to low Raman intensity ratio ($I_G/I_D \sim 1$). Nonetheless, the NBD pattern indicates that crystallites are aligned parallel to the fiber axis (see the inset of Fig. 1(a3)), which leads to an expression of mechanical anisotropy. On the other hand, the structure of the pitch-based carbon fiber possesses the parallel arrangement carbon crystallite
microtexture in the axial direction (Fig. 1(b3)). Additionally, their $I_G/I_D$ ratio is approximately 10. These results suggest that the graphitic sheets are almost perfectly aligned with the fiber axis, which may be attributable to the degradation of indentation modulus in the 45° and radial direction compared with the PAN-based carbon fiber. For the axial direction of the pitch-based carbon fiber, even though the crystallite diameter and length were large, they exhibited the zigzag microtexture, and additionally, some voids were also observed. These features are also visible in the TEM images shown in Fig. 1(b2) and (b3). Thus, during the indentation in axial direction, the crystallites not only were compressed elastically in the axial direction but also may bend and buckle, resulting in the comparable indentation modulus to the PAN-based carbon fiber.

It is known that the tensile moduli (i.e. Young’s modulus in the axial direction, $E_f$) of T700SC and K13D carbon fibers are 234 GPa and 940 GPa, respectively (Naito, et al., 2017). The indentation modulus measured in the axial direction is fairly different from the corresponding tensile modulus, and cannot be identified with it for such highly anisotropic materials such as carbon fibers. This difference is mainly due to nano-buckling of graphene layers as mentioned above. When the indentation load was applied on transversal cross section, the carbon fiber was subjected to a tensile stress state normal to the indentation direction simultaneously. The tensile stress can further weaken the bonding between graphene layers and enhance the buckling effect (Duan, et al., 2019). Such buckling can lead to a
decrease in stiffness because the graphene layers bend and can no longer carry the indentation load. On the other hand, Csanádi et al. (2017) showed that the indentation modulus measured along the transversal direction is similar to the transverse elastic modulus ($E_T$). Thus, supposing that the indentation modulus in the radial direction is the same as the transverse elastic modulus, the anisotropy of elastic modulus ($E/E_T$) of the PAN- and pitch-based carbon fibers is calculated to be 11 and 165, respectively (shown in Table 1). $E/E_T$ of the pitch-based carbon fiber is approximately 15 times as high as that of PAN-based carbon fiber, suggesting that the pitch-based carbon fiber possesses a large mechanical anisotropy. The relationship between $E_T$ and $E_i$ of carbon fibers evaluated in this study and measured with nanoindentation, compression tests and resonant ultrasound spectroscopy (RUS) presented in the literature are shown in Fig. 6. The transverse elastic modulus of the PAN-based (T700SC) carbon fiber studied in this study is in the same range as those for other fibers measured with nanoindentation and RUS technique presented in the literature (Maurin, et al., 2008; Csanádi, et al. 2017; Tane, et al., 2019). The transverse elastic modulus decreases exponentially with increasing tensile modulus regardless of the evaluation method. Even though the $E_T$ values measured from compression tests (Naito, et al., 2017) are significantly smaller, the slope of the regression line approximately coincides with that for nanoindentation. From the above, we can conclude that the nanoindentation technique is useful tool to characterize the mechanical anisotropy of pitch-based carbon fibers, and the mechanical anisotropy observed in the carbon fibers increases with their crystallinity and $E_i$ regardless of the synthesis method. In view of the significance of structural and mechanical anisotropy of carbon fibers, further studies should be carried out to examine the structural–mechanical property relationships of carbon fibers.

Table 1 Anisotropy of elastic modulus of carbon fibers calculated by the tensile modulus and transverse elastic modulus which is assumed to be the as the indentation modulus in the radial direction ($M_T$). $E/E_T$ of the pitch-based carbon fiber is approximately 15 times as high as that of PAN-based carbon fiber.

|                | T700SC | K13D |
|----------------|--------|------|
| Tensile modulus, $E_i$ (GPa)$^a$ | 234    | 940  |
| Transverse modulus, $E_T \approx M_T$ (GPa) | 20.9   | 5.7  |
| Anisotropy of elastic modulus ($E/E_T$) | 11     | 165  |

$^a$: Naito, et al., (2017)

Fig. 6 Relation between transverse modulus and tensile modulus for PAN-based and pitch-based carbon fibers. The solid lines are regression lines provided by the least-squares regression analysis. The transverse modulus of carbon fibers decreases exponentially with increasing tensile modulus regardless of the evaluation method.
4. Conclusions

In this study, carbon fiber/epoxy composites made with the pitch-based carbon fiber as well as PAN-based carbon fiber were prepared, and the crystallinity, nanostructures and mechanical anisotropy of the carbon fibers were investigated by the SEM, TEM, Raman spectroscopy and nanoindentation. It was shown that the indentation modulus decreased with a decreasing orientation angle from axial to radial direction. The pitch-based carbon fiber in the axial direction exhibited a similar indentation modulus in comparison to the PAN-based carbon fiber for the same orientation, whilst the indentation moduli of the pitch-based carbon fiber in the 45° and radial direction were smaller than those of PAN-based carbon fiber. Supposing that the indentation modulus in the radial direction was same as the transversal elastic modulus, the anisotropy of elastic modulus \( E_f/E_T \) of the PAN- and pitch-based carbon fibers was calculated to be 11 and 165, respectively. \( E_f/E_T \) of the pitch-based carbon fiber was approximately 15 times as high as that of PAN-based carbon fiber, suggesting that the pitch-based carbon fiber possessed a large mechanical anisotropy. The higher mechanical anisotropy observed in the pitch-based carbon fiber was mainly due to the existence of the parallel arrangement carbon crystallite microtexture with high crystallinity in the axial direction. Indeed, the pitch-based carbon fiber exhibited the Raman intensity ratio \( I_G/I_D \) of approximately 10, which was higher than that of PAN-based carbon fibers \( I_G/I_D \sim 1 \). Our findings suggested that combining a SEM, TEM and Raman spectroscopy data with the nanoindentation technique is useful tool to characterize the mechanical anisotropy of pitch-based carbon fibers as well as PAN-based carbon fibers.

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