Synchrotron microbeam X-ray diffraction system provides an important hint for developing better carbon fiber

Carbon fiber is now being applied in much wider fields including in the main structure of jet airplanes, the propellers of wind power generators, the main bodies of automobile cars, and so forth. In this sense, it is therefore necessary to further improve the physical properties of carbon fiber enable its use in a wider range of application with higher reliability. However, current commercial carbon fiber products include a contradiction regarding their mechanical properties: a carbon fiber with higher fracture strength has a lower Young's modulus along the fiber direction, whereas a fiber with a higher Young's modulus possesses lower strength. A higher strength means that the carbon fiber can safely support a heavier weight, whereas a material with a higher Young's modulus is more resistant to instantaneous mechanical deformation. In other words, an ideal carbon fiber should have the mechanical properties of the highest possible fracture strength and the highest possible Young's modulus, which may result in extreme robustness even for the case of a strong externally applied mechanical stimulus.

How can we develop such an ideal carbon fiber? One solution is to clarify the mechanical deformation behavior of a carbon fiber by focusing on the crystalline part. As is well known, a carbon fiber has a complicated aggregation structure of crystalline and amorphous regions, as shown in Fig. 1, in which graphite meshes are stacked together to form a relatively regular crystalline region. When an external tensile force is applied, the graphite network is deformed, which can be traced by measuring the shift of the corresponding X-ray diffraction peak. Since the crystalline region may be assumed to take essentially the same structure, mechanical deformation may be common among the various types of sample produced under different preparation conditions, for example, with different heat-treatment temperatures at which the original poly(acrylonitrile) fiber (precursor) is annealed to transform it to the carbon fiber with higher quality. A carbon fiber prepared in this manner was set in a stretching device and the WAXD pattern was measured under tension. The strain of the deformed crystal lattice was evaluated from the shift of the diffraction peak. On the other hand, the stress applied to the crystal region cannot be found directly, and therefore a serious assumption must be made that the stress acts homogeneously throughout the sample. The plot of stress versus strain gives a straight line in an infinitesimally small deformation region, the slope of which gives the Young's modulus. The thus-estimated Young's modulus of the crystalline region is called the apparent crystallite modulus (E_c^{app}) since a homogeneous stress distribution is assumed. As mentioned above, E_c^{app} should be common to samples prepared under various conditions as long as the assumption of a homogeneous stress distribution is reasonable. If the E_c^{app} value varies among the samples, then it must be concluded that the local stress acting on the crystalline region is different depending on the sample morphology. This means that the assumption of a homogeneous stress distribution cannot be employed anymore and that the heterogeneous stress distribution must be evaluated quantitatively [1,2]. This concept has been verified for the case of carbon fiber. It is also necessary to know the difference in the stress distribution among the various local parts of the fiber. This can be determined by performing X-ray diffraction measurement with an X-ray microbeam incident on a monofilament of about 6 μm diameter under the application of a tensile force. Such an experiment requires high accuracy and was successfully performed for the first time by utilizing a microbeam X-ray diffraction system coupled with a highly sensitive CCD detector at beamlines **BL47XU** and **BL03XU** [3,4]. The X-ray measurement was made

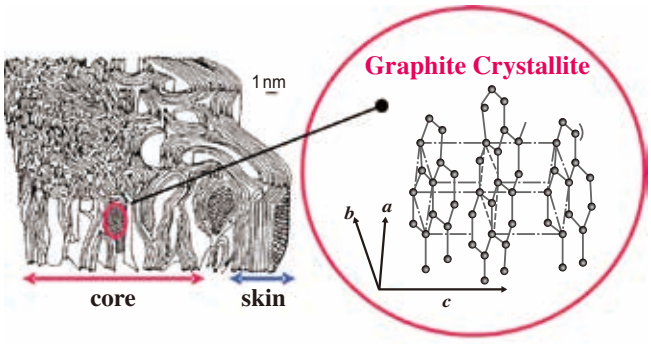

Fig. 1. Schematic illustration of inner structure of carbon fiber.

along the width direction at intervals of 0.2 μm using a beam of 0.5 μm radius. The results were as follows: (i) The E_c^{app} value was appreciably different among various samples. (ii) E_c^{app} was almost the same at various positions of a monofilament with a low Young's modulus (252 GPa), while it was largely different between the skin and core parts of a monofilament with a higher Young's modulus (445 GPa).

Similar measurements were also carried out to obtain the Raman spectra of the samples [5]. The tensile force deforms the net plane structure of graphite and the related vibrational bands are shifted to same extent. In the case of measuring the Raman spectra, however, an incident laser beam is absorbed by a black carbon fiber, and information is only obtained for the mechanical deformation on the outermost surface to a depth of several tens of nanometers. Also, it was found that the observed band shift in Raman spectra was different among the samples with various preparation histories.

Both the X-ray and Raman scattering data clearly indicated that the stress is not homogeneously distributed among the crystalline, amorphous, and outermost surface parts. A complex mechanical model was built up to interpret these experimental data quantitatively, which consisted of an inner fiber and an outermost surface. As illustrated in Fig. 2, the inner part (skin and core) consists of serially arrayed mechanical elements representing crystalline (C2) and amorphous (A) regions and a parallel element representing the crystalline region (C1). *a* and *b* in this figure are the fractions of these mechanical elements. The outermost surface was also taken into account in the theoretical derivation of the mechanical equations. Although the details are omitted here, the values of *a* and *b* in Fig. 2 were determined on the basis of the above-mentioned experimental data, from which the distribution of stress was estimated as schematically illustrated in Fig. 3 [4]. For example, in the case of a carbon fiber sample with a 445 GPa Young's modulus, an externally applied stress is concentrated on the outermost surface. If a tiny point of mechanical weakness exists on this surface (a structural defect such as a void, kink, or misoriented crystalline region), it may easily cause a breakage starting from the surface part. On the other hand, the sample with a lower Young's modulus of 255 GPa is mechanically tough because the stress concentration occurs mainly on the parallel mechanical element inside the fiber. In this way, we have achieved a breakthrough in clarifying the contradictory mechanical properties regarding the toughness and hardness of carbon fiber [4]. A carbon fiber with excellent mechanical properties must possess as homogeneous structural distribution as possible over the cross section of the fiber. Although our achievement is only a starting point, it provides a quantitative basis for the production of carbon fiber with superior mechanical properties.

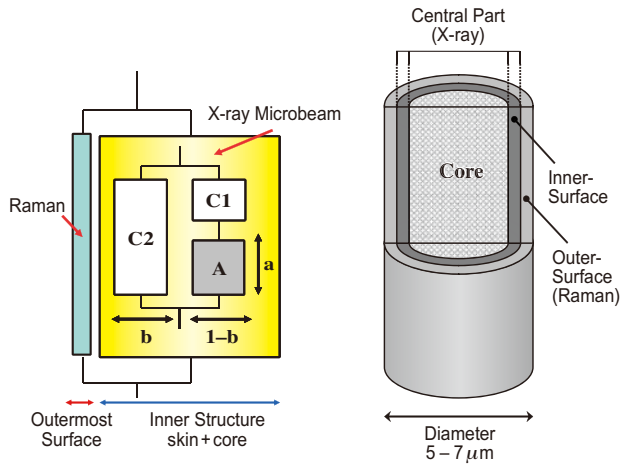

Fig. 2. Carbon fiber and complex mechanical model.

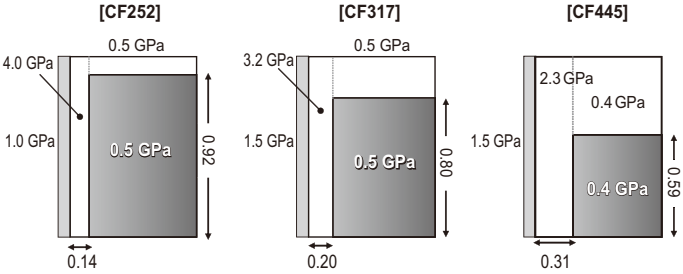

Fig. 3. Stress distribution among various mechanical elements of carbon fibers with different Young's moduli, where each fiber is subjected to a bulk tensile stress of 1 GPa.

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