Maximum available tensile strength of carbon fibers

Masatoshi Shioya[1]*, Takashi Kajikawa[1], Kuniaki Takahashi[1], Yoshiki Sugimoto[2]

[1]*School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-S8-34 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*
[2]*Structural Materials Research Institute, The National Institute of Advanced Industrial Science and Technology, 2266-98, Anagahora, Shimoshidami, Moriyama-ku, Nagoya, Aichi 463-8560, Japan*

*Corresponding author

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Abstract

Development of carbon fibers from alternative precursory materials through new production processes is a recent topic of active research. In such a research, the maximum available tensile strength, i. e. the tensile strength which will be achieved after elaboration to suppress defect formation during production process, is the matter of great concern. We have developed a method for determining this strength through the tensile test on a single fiber after introducing an artificial notch. In the present paper, this method has been refined. By using the refined method, the distribution of the maximum available tensile strength at various radial positions has been measured for a polyacrylonitrile-based carbon fiber. The difference between the maximum available tensile strength and the strength predicted using other methods such as those based on the fracture toughness and the fiber-length dependence of the tensile strength has also been discussed. Copyright © 2018 VBRI Press.

Keywords: Carbon fiber, tensile strength, defect, crack.

Introduction

Development of carbon fibers (CFs) from alternative precursory materials through new production processes aiming at cost reduction, production efficiency improvement and further performance improvement is a recent topic of active research on the background of expanding application fields to automobile and energy generating sectors for reducing carbon dioxide emission. In such a research, the tensile strength which will be achieved after elaboration to suppress defect (initial crack) formation during production process is the matter of great concern (**Fig. 1**). This strength is exerted by the structure of the actual fiber under investigation but with the absence of initial crack, rather than the ideal fiber structure which theoretically maximizes fiber strength. We have called this tensile strength 'maximum available tensile strength (MATS)' and developed a method for determining it through the tensile test on a single fiber after introducing an artificial notch.

With the ordinary tensile test on the unnotched fiber, the fiber breaks from the initial crack with unknown shape and size, while with the tensile test on the notched fiber, the fiber breaks at the notched cross section and the maximum tensile stress actually sustained by the material at the notch tip can be determined by using the stress concentration factor calculated from the shape and size of the artificial notch.

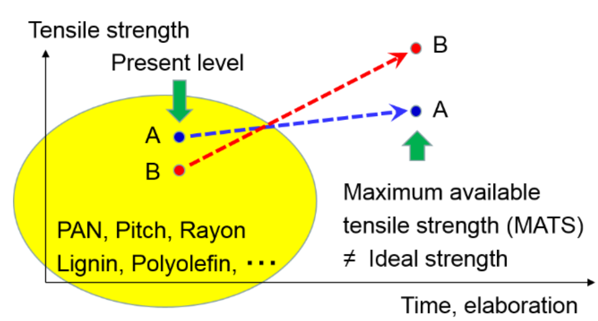

Fig. 1. The concept of the maximum available tensile strength.

In the present paper, this method has been refined by taking account of the shapes of the fiber and the notch. By using the refined method, the distribution of the MATS at various radial positions has been measured for a polyacrylonitrile(PAN)-based CF. The difference between the MATS and the strength predicted using other methods such as those based on the fracture toughness and the fiber-length dependence of the tensile strength has also been discussed.

Experimental

A PAN-based CF with the Young modulus of 235 GPa, the average single-fiber tensile strength (SFTS) of 4.1 GPa at a gage length of 10 mm, the density of 1.8 g cm^{-3}, and the diameter of 7.1 μm was used in the present study.

The single-fiber tensile strength of the notched fibers were measured according to the following procedure as described in a previous paper [1]: A single CF was bonded on a paper template across a rectangular window, sputtered with a gold layer for obtaining the electrical conductivity through the template and processed with a focused ion beam milling apparatus (FIB, **Fig. 2(a)**) for introducing the artificial notches having flat surfaces perpendicular to the fiber axis as shown in **Figs. 2(b)** and **2(c)**. The fiber diameter and notch depth were measured using the scanning ion microscopy (SIM) images obtained with the FIB system. The radius of curvature of the notch tip was in the range from 0.08 to 0.20 μm. The single-fiber tensile tests of notched CFs were performed at a gauge length of 6 mm and a strain rate of 2% min^{-1}. **Fig. 2(d)** shows the fracture surface of the notched CF. Radial striations running from the center of the notch tip can be found, which confirms that the notched fiber started to break from the center of the notch tip.

Analysis

The tensile stress of the notched fiber at the notch tip, σ_m, and that in the region far distant from the notch, σ_b, when the fiber starts to break are related as

$$\sigma_m = \alpha \sigma_b \tag{1}$$

where α is the stress concentration factor. The MATS is given as σ_m. In the previous paper [1], the stress concentration factor for a semi-infinite plate having a U-shaped notch was approximately used. For refinement, the stress concentration factor for a cylinder having a notch whose tip is elliptical when seen perpendicularly to the fiber axis and straight when seen in parallel to the fiber axis, represented by the following equations is used in the present study.

$$\alpha = Y\left(1 + 2\sqrt{\frac{a}{\rho}}\right) \tag{2}$$

$$Y = 0.99 - 0.61\left(\frac{a}{D}\right) + 5.66\left(\frac{a}{D}\right)^2 - 0.16\left(\frac{a}{D}\right)^3 \tag{3}$$

where D is the fiber diameter, a the notch depth, ρ the radius of curvature of the notch tip, and Y the geometric constant. Eq. 3 represents the geometric constant at the center of the notch tip where the tensile stress reaches maximum.

It has been shown that the stress field equations around an elliptic hole or a hyperbolic notch are similar to those around a crack having a sharp edge in the region far distant from the notch tip or the crack edge as compared with ρ [2]. This allows to use the same geometric constant for the corrections of the stress concentration factor and the stress intensity factor where the former determines the stress field equations around a blunt hole or notch and the latter determines those around a sharp crack. By applying this approximately to the stress fields near the notch tip, the geometric constant derived for the correction of the stress intensity factor given by Eq. 3 [3] was used for the correction of the stress concentration factor in Eq. 2. At $Y = 1$, Eq. 2 gives the stress concentration factor for an infinite plate with an elliptic hole [4].

Further refinement of calculation of the stress field can be performed by taking account of the anisotropy in the elastic constants for CFs [5]. However, this is not performed in the present study since only the Young modulus was measured among various elastic constants.

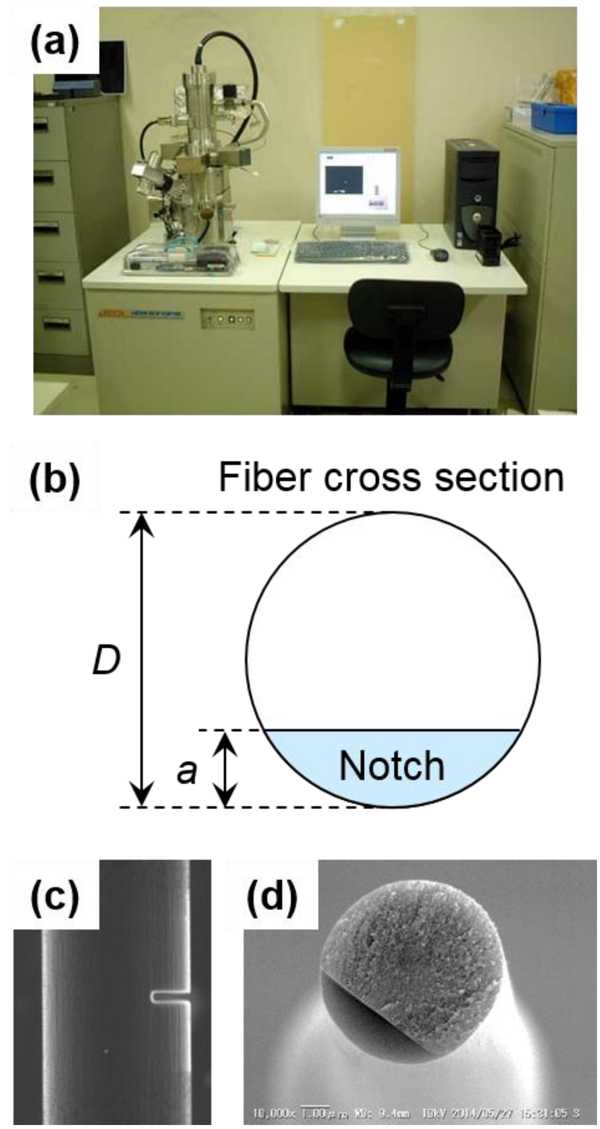

Fig. 2. (a) FIB at Ookayama Materials Analysis Division, Technical Department in Tokyo Institute of Technology, (b) Schematic of notched fiber cross section, (c) SIM image of notched CF, and (d) Tensile fracture surface of notched CF.

Results

The SFTS of the notched CFs was measured at various notch depths [6]. **Fig. 3(a)** shows the MATS calculated from the SFTS using the stress concentration factor of Eq. 2, as a function of the normalized radial position which is 0 at the fiber center and 1 at the fiber surface. It can be found that the MATS at the central part of this

CF is lower than the tensile strength of the unnotched fiber, but it increases towards fiber surface and is far superior to the tensile strength of the unnotched fiber near the fiber surface.

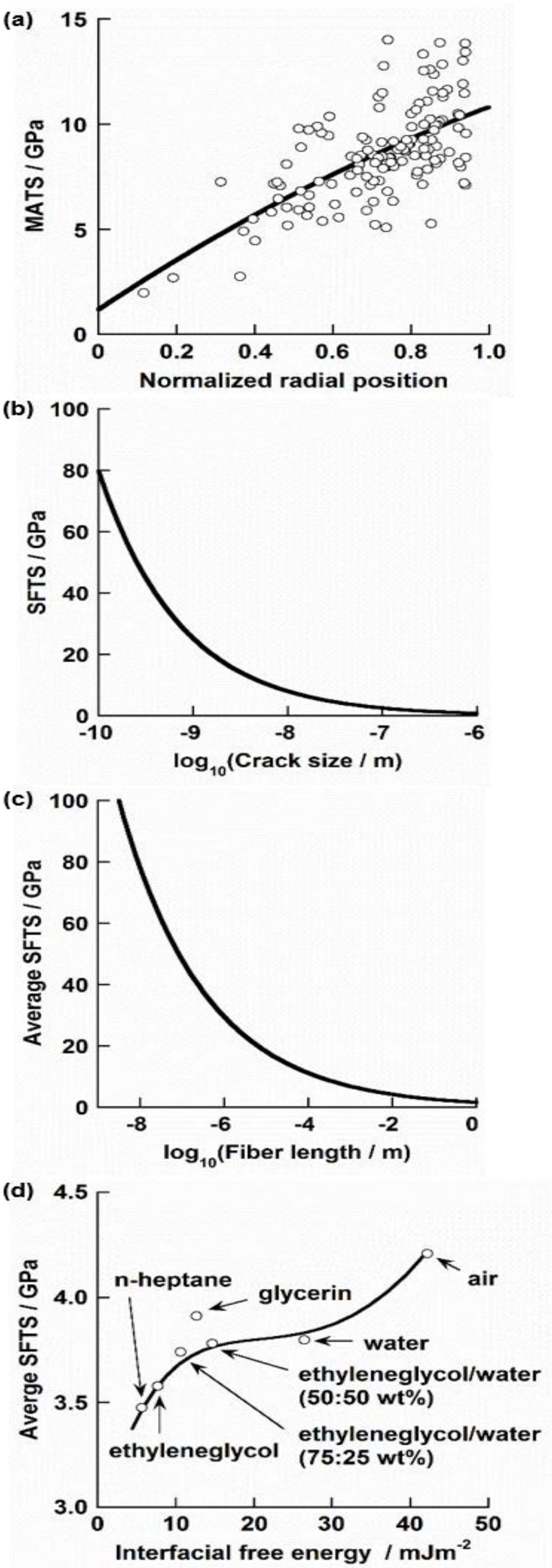

Fig. 3. (a) MATS vs. normalized radial position for a PAN-based CF, (b) SFTS vs. initial crack diameter, (c) Average SFTS vs. fiber length, and (d) Average SFTS measured in various test media vs. interfacial free energy between CF and test media.

Discussion

Prediction of the tensile strength of CF achieved by reducing the crack size can be made using the equation from the linear fracture mechanics,

$$\sigma_b = \frac{K_{Ic}}{Y}\sqrt{\frac{2}{\pi c}} = \frac{1}{Y}\sqrt{\frac{4E\gamma}{\pi c}} \tag{4}$$

where σ_b is the tensile strength of a material having a crack with the diameter c, E the Young modulus, K_{Ic} the mode-I fracture toughness, γ the free energy of crack surface, and Y the geometric constant. The fracture toughness of CFs can be determined based on Eq. 4 from the SFTS and the size of the initial crack observed in the fracture surface [7, 8]. Then the tensile strength of a CF having a crack of any size can be predicted using this equation. **Fig. 3(b)** shows the tensile strength of a CF predicted with this method using a reported value of 1 MPa $m^{1/2}$ for K_{Ic} [8] and the assumed value of $Y = 1$, as a function of the initial crack diameter.

Another method for predicting the tensile strength of CF achieved by reducing the crack size is based on the fiber-length dependence of the tensile strength. As the fiber length decreases, the fiber strength increases since the probability that the fiber contains cracks decreases. The decrease in this probability is the larger for the larger cracks since the amount of the larger cracks is smaller than that of the smaller cracks. This is because the number density of the cracks which break at a given stress increases exponentially with increasing stress with the Weibull distribution shown below, and the smaller cracks break at a higher stress. Therefore, the reduction in the fiber length corresponds to the reduction in the size of the cracks contained in a single fiber. The stochastic nature of the location of the cracks causes distribution in the SFTS. With the fibers whose SFTS distributes according to a two-parameter Weibull distribution [9],

$$F(\sigma_b) = 1 - \exp\left(-\frac{L}{L_0}\left[\frac{\sigma_b}{\sigma_0}\right]^m\right) \tag{5}$$

the average SFTS, $\langle\sigma_b\rangle$, at the fiber length L is given by

$$\langle\sigma_b\rangle = \sigma_0 \Gamma\left(\frac{1}{m}+1\right)\left[\frac{L}{L_o}\right]^{-1/m} \tag{6}$$

where F is the number fraction of the single fibers having the SFTS σ_b or less, m the shape parameter, σ_0 the scale parameter, and L_0 an arbitrarily chosen reference length for making σ_0 unitless. The Gamma function can be approximated as

$$\begin{aligned}\Gamma(x+1) &\approx 1 - 0.575x + 0.951x^2 - 0.700x^3 \\ &+ 0.425x^4 - 0.101x^5 \quad (0 \le x \le 1)\end{aligned} \tag{7}$$

The parameters m and σ_0 can be determined from the slope and the intercept of the plot of ln[-ln(1 - F)] vs. ln σ_b (Weibull plot). Then the fiber-length dependence of the average SFTS can be calculated using Eq. 6. The crack size which corresponds to the average SFTS can be known from Eq. 4. The Weibull parameters for the unnotched CF used for the present study were m = 4.7 and σ_0 = 1.7 GPa. **Fig. 3(c)** shows the average SFTS calculated with Eq. 6 using these values as a function of the fiber length.

Figs. 3(b) and **3(c)** show that the fiber strength predicted with both of the above methods diverges to infinity at extremely small initial crack size or fiber length. These predictions are, however, incorrect because of the following reason: From a microscopic point of view, the tensile fracture is the process to separate pairs of atoms from the equilibrium distance to infinity. This process can be completed only when all of the energy, the stress, and the strain required for separating atoms to infinity can be applied from the environment. The fracture takes place at the moment when all the requirements are satisfied and the one which is finally satisfied determines the fracture criterion. In the case that there are several possible ways of tensile fracture, the one which takes place at first in the tensile process determines the way of actual fracture.

In the tensile process of a CF having a sharp and relatively large initial crack, the stress requirement is satisfied long before the energy requirement is satisfied due to the large stress concentration at the crack tip, and the crack only starts to grow when the energy requirement is also satisfied (energy criterion). On the other hand, if the crack is extremely small, the tensile fracture takes place in the region without containing the crack at the moment when the stress requirement is satisfied (stress criterion) since the fracture from the crack tip requires much larger tensile stress. The MATS indicates the strength when the CF breaks in the region without containing the crack. Therefore, the tensile strength of CFs without containing the crack does not diverge to infinity but is limited by the MATS.

Whether the tensile fracture of CFs is governed by the energy criterion or the stress criterion can be judged by comparing the SFTS in air and liquids. We have reported that PAN-based CFs show lower tensile strength in liquids as compared with the strength in air as shown in **Fig. 3(d)** [1]. The strength reduction in liquids is considered to take place due to the decrease in γ by the contact of the crack surface with the liquid or its vapor. Such strength reduction takes place only when the tensile fracture is governed by the energy criteria and Eq. 4 is valid. For the notched CFs, the tensile reduction in liquids did not take place [1] which confirmed that tensile fracture of CFs having artificial notches with the shape and sizes used in this study was governed by the stress criterion. It is also possible to determine the ratio of the numbers of the surface and the internal cracks from the degree of the strength reduction in liquids [1].

The estimation of MATS is useful for selecting the precursory materials which have the potential to exert a high tensile strength. In order to realize the fibers possessing the strength reaching to MATS, it is essential to find out a method to suppress the defect formation during production process. However, even if such a method cannot be found out, searching for the fibers possessing a high value of MATS is meaningful since the large MATS can be utilized as the strength of composites if a strong interfacial bonding can be established. The required level of interfacial bonding is determined by the number density of the defects and the target value of the strength.

Conclusion

A refined method for determining the MATS of CFs was shown. By using the refined method, the distribution of the MATS at various radial positions was measured for a PAN-based carbon fiber. Searching for the fibers possessing a high value of MATS is meaningful since the large MATS can be utilized as the strength of composites if a strong interfacial bonding can be established even if a method to suppress the defect formation during production process cannot be found out.

Acknowledgements

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References

1. Shioya, M.; Inoue, H.; Sugimoto, Y.; *Carbon,* **2013**, *65*, 63.
2. Creager, M.; P. C. Paris; *Int. J. Fract. Mech.*, **1967**, *3*, 247.
3. Morishita, K.; Ochiai, S.; Okuda, H.; Inshikawa, T.; Sato, M.; Inoue, T.; *J. Am. Chem. Soc.*, **2006**. *89*, 2571.
4. Inglis, C. E.; *Transactions of the Institute of Naval Architects*, **1913**, *55*, 219.
5. Sugimoto, Y.; Shioya, M.; Kageyama, K.; *Carbon*, **2016**, *100*, 208.
6. Shioya, M.; Hayashi, K.; Sugimoto, Y.; Kobayashi, T.; Abstracts of paper, *41th Annual Meeting of The Carbon Society of Japan*, 2C10, **2014**.
7. Matsuo, Y.; Yasuda, K.; Kimura, S.; *J. Ceram. Soc. Japan.*, **1990**, *98*, 389.
8. Honjo, K.: *Carbon*, **2003**, *41*, 979.
9. Weibull, W.; *J. Appl. Mech.*, **1951**, *18*, 293.

