Tensile Strength and Its Variation of PAN-Based Carbon Fibers. I. Statistical Distribution and Volume Dependence

Weidong Yu,[1,2] Jiangwei Yao[1]

[1]*College of Textiles, Donghua University, Shanghai 200051, China*
[2]*Wuhan University of Science and Engineering, Wuhan 430074, China*

Received 23 August 2005; accepted 3 October 2005
DOI 10.1002/app.23399
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effects of the diameter, gauge length, and volume of carbon fibers on the tensile properties and their variation are discussed on the basis of the weak-link theory and Weibull distribution in a single-filament test. As far as variation is concerned, the stress of carbon fibers should be obtained by the division of the force not by the mean cross section of all the fibers but by the cross section of individual fibers because of the diameter variation. The volume effect of carbon fibers influences not only the mean of the tensile properties but also their variation. The experimental results indicate that the volume dependence in the radial direction is much bigger than that in the axial direction. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3175–3182, 2006

Key words: fibers; fracture; mechanical properties

INTRODUCTION

Carbon fibers are high-performance fibers widely used as reinforcements in composites. The mechanical behavior of fiber-reinforced composites is dependent, to a great extent, on the tensile properties of the reinforcing fibers. Therefore, the tensile strength of carbon fibers is the most important factor for the strength of their composites. However, the tensile strength of carbon fibers shows a large scatter and remarkable size dependence.[1] Therefore, it cannot be described with a mean value only;[2] the variation of the carbon-fiber strength is more important in characterizing the tensile properties of carbon fibers.

In fact, the strength of carbon fibers, as described by Griffith's theory, depends on various flaws or, more precisely, the worst flaw (if the failure of carbon fibers is caused by a single flaw) or a combination of the worst flaws (if the failure of carbon fibers is caused by several flaws) that exist in the fibers. If the part of the fiber in which the worst flaw or a combination of the worst flaws lies is the weak link or the weakest link, the fracture of the carbon fibers relies only on the strength of the fiber weak link (FWL). The severity and structure of FWLs are the fundamental factors that influence the tenacity, strength variation, or distribution of carbon fibers.[3]

Because the occurrence of flaws within a fiber is random by nature, the probability of encountering a severe FWL becomes greater as the sample volume increases. The inverse dependence of the tensile strength on the sample volume has been reported. Moreton[4] stressed the tensile strength of carbon fibers at different gauge lengths in his experiments. The results showed that the strength of carbon fibers with the same diameter decreased with an increase in the specimen length. Tetsuy and Takashi[5] found that the strength of carbon fibers was dependent not only on the fiber length but also on the fiber diameter and that the size dependence of the strength in the radial direction was 10 times larger than the dependence in the axial direction.

On the other hand, it is well known that tensile testing carbon fibers is quite difficult, and very high variation partly results from the test itself because of the brittleness of carbon fibers. Because of the influence of the experimental operation and adhesive effect, the actual gauge length is not the same as the set one; that is, there is variation of the gauge length. Meanwhile, the diameter is different from fiber to fiber; the measurement of the fiber profile is advised.

The variation of the strength of carbon fibers can be characterized by its distribution. The large number of experimental data in carbon-fiber tensile tests indicates that if the volume of all the sample is the same, the strength distributions of the carbon fibers can be fitted to a two-parameter Weibull function,[1,6,7] which is based on the assumption that all the samples have the same volume and form:

$$P = 1 - \exp\left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \tag{1}$$

Correspondence to: W. Yu (wdyu@dhu.edu.cn).

where P is the cumulative failure probability of a fiber at a stress less than or equal to stress σ, σ_0 is the scale parameter, and m is the Weibull shape parameter that describes the variability of the failure strength. The rearrangement of the Weibull cumulative expression gives the following equation:

$$\ln \ln\left(\frac{1}{1-P}\right) = m \ln \sigma - m \ln \sigma_0 \tag{2}$$

Then, the scale and shape parameters can be obtained from the linear fitting of ln ln$[1/(1 - P)]$ and ln σ. However, there exist different sorts of flaws in carbon fibers; on the basis of tests of the strength of fibers over a wide range of lengths, Pickering and Murray[7] suggested that a higher order Weibull expression should be adopted:

$$P = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_{0(1)}}\right)^{m_1} - \left(\frac{\sigma}{\sigma_{0(2)}}\right)^{m_2}\right] \tag{3}$$

To understand the effect of flaws on the tensile strength, the effect of the volume variation on the stress variation must be considered, especially for large diameter variations. In this work, tensile tests of single carbon fibers were performed to determine the relationship of the diameter and gauge-length variation of fibers with the strength distribution and its variation on the basis of the weak-link theory and Weibull distribution.

EXPERIMENTAL

Carbon fibers

The polyacrylonitrile (PAN)-based carbon fibers used for this investigation, with an average diameter of 7.0 μm, were in bundles of 12,000 filaments. To ensure the consistency of the measurements, all the fibers were taken from the same bundle.

Tensile tests

Single-fiber samples randomly selected from the same fiber bundle were fixed by an epoxy resin on paper window cards without pretension. The fibers were aligned straight along the central axis of the card to ensure that the axis of the carbon fibers was parallel to the direction of stretching. The schematic diagram for the sample preparation is shown in Figure 1. The fiber length between the adhesive points is called the gauge length; it was 15, 30, and 40 mm for the tensile tests. The adhesive points had to be strong enough to ensure that the carbon fiber would not be pulled out during the stretching process.

The cross-sectional area was evaluated from the minimum fiber diameter, which was measured at the narrow part of the fiber for more than 10 points per 0.1 mm or at 1 point per millimeter if the fiber was even in diameter by microscopy for each of the samples one by one before the tensile test.

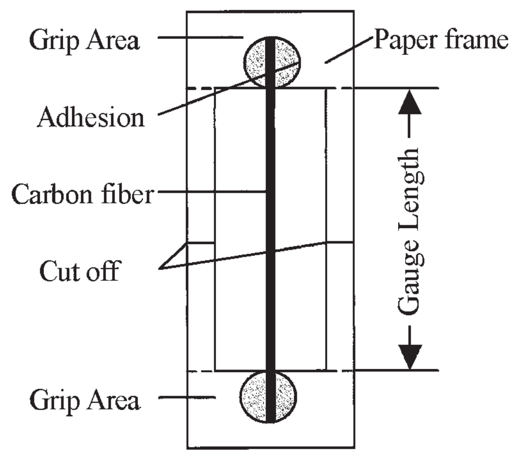

Figure 1 Specimen with paper window cards.

The specimen with the paper card was mounted to clamps of a tensile tester and cut off the paper frame, as shown in Figure 1; the fiber was then extended to failure at the downward speed of 5 mm/min. The force–elongation curve for each measurement was recorded, and the corresponding stress–strain (σ–ε) curve was calculated according to the minimum diameter measured and the actual gauge length; it was drawn as illustrated in Figure 2.

ANALYTICAL PROCEDURE

According to the stress–strain curve, the failure stress (σ_b) and strain (ε_b) can be obtained as eqs. (4) and (5), respectively:

$$\sigma_b = \frac{4F}{\pi d^2} \times 10^{10}\ \text{(GPa)} \tag{4}$$

$$\varepsilon_b = \frac{\Delta L - OO' - C_s F}{GL + OO'} \times 100\% \tag{5}$$

where F is the force of the fiber in stretching; d represents the minimum diameter of the fiber; C_s is the system compliance, which is the elongation resulting from a load-weighing system, clamps, and grip penetration per unit of force; ΔL is the absolute displacement of one of the clamps, so the fiber elongation is equal to $\Delta L - OO'$; GL is the actual gauge length and OO' is the displacement for the fiber straightening.

Because the stress–strain curve of carbon fibers is almost linear, as shown in Figure 2, the initial modulus (E) can be calculated with eq. (6):

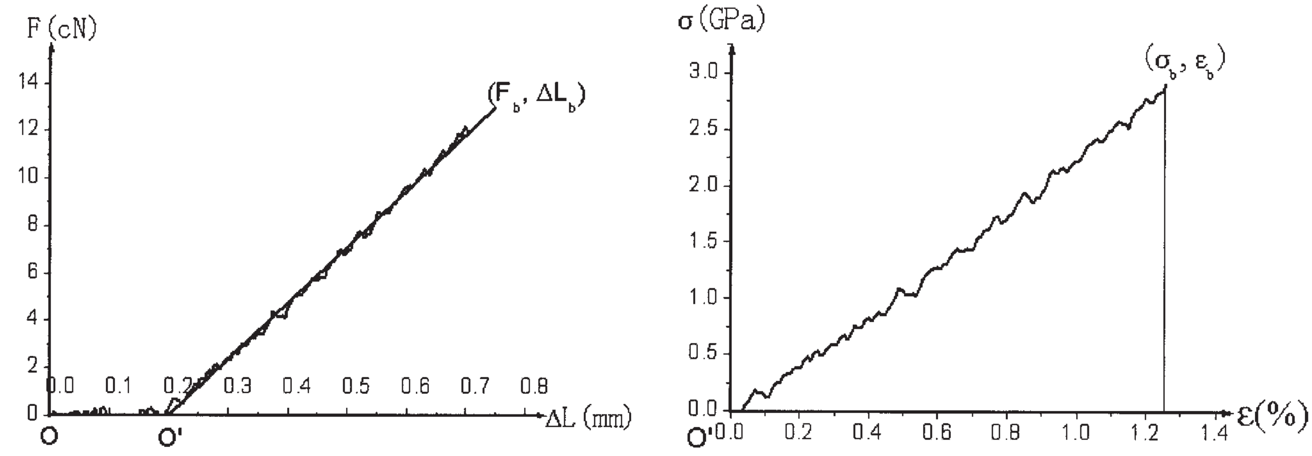

Figure 2 Calibration of the carbon-fiber strain.

$$E = \frac{\sigma_b}{\varepsilon_b}\ (\mathrm{GPa}) \tag{6}$$

RESULTS AND DISCUSSION

Coincidence between the measured and theoretical distributions

Measured distribution and fitting distributions

Although a Gaussian distribution is often used to express the strength distribution of flexible fibers, the Weibull function indeed fits the strength distribution of carbon fibers better than a Gaussian distribution because of the brittleness of carbon fibers. So far, the Weibull expression has been widely adopted to discuss the strength of carbon fibers. The Weibull distribution is a versatile distribution that can take on the characteristics of other types of distributions according to the value of its shape parameter. When m is equal to 1, 2, or 3.57, it represents the exponential, Raleigh, or Gaussian (normal) distribution, respectively. To verify the statistical distribution of the carbon-fiber tensile property, the fittings of Gaussian and Weibull distributions were carried out. The corresponding correlation coefficients are listed in Table I. The results in Table I show that a Weibull distribution for tensile properties F, σ_b, and E is more fitting than a Gaussian distribution, except for ε_b.

Figure 3 presents Weibull plots for the force, stress, strain, and modulus distribution of carbon fibers. The best fit straight lines in the Weibull plots, used to calculate the Weibull parameters, are also shown.

TABLE I
R^2 Values of Different Fittings of Carbon-Fiber Tensile Properties

	F	σ_b	E	ε_b
Gaussian distribution	0.8925	0.9249	0.8899	0.9705
Weibull plots	0.9918	0.9958	0.9859	0.9195

Relationship between the measured data and the parameters of the weibull distribution

σ_0 is also called the characteristic strength because it is the tensile strength at which $1 - e^{-1}$ (ca. 63%) of the sample fractures (P is $1 - e^{-1}$). m is equal to the slope of the Weibull plot, so it is called the Weibull slope too. m provides a measure of scatter in the distribution, in that the amount of scatter is inversely proportional to m.

In Table II, CV_{0m} is the measured coefficient of variability (CV) value; χ_0 represents the Weibull scale parameters F_0, σ_0, E_0, and ε_0; χ_{0m} stands for the tensile parameter measured when P is $1 - e^{-1}$; and Δ is the difference rate between the measured value and theoretical distribution parameters {i.e., Δ (%) = [(Measured value − Theoretical value)/Measured value] × 100}. Because there is no accurate equation expression between m and CV, the linear fit for $1/m$ and CV_{0m} is given here (Fig. 4). Both Δ in Table II (4.11%)and the linear fit show that the strain of the carbon fiber did not fit a Weibull distribution well, and this agrees with the R^2 values of the Weibull plot in Table I.

Comparison of the distributions of carbon fibers

The distribution of the fiber strength is usually described by the Weibull equation [eq. (1)]; little is known about the strain and modulus distribution. As we can see from Figure 3, the modulus, force, and stress distribution fit a Weibull distribution better than a Gaussian distribution, so we think the modulus distribution and stress distribution can be described by a Weibull distribution. As for the strain distribution, the fitting result of Gauss plots is better than that

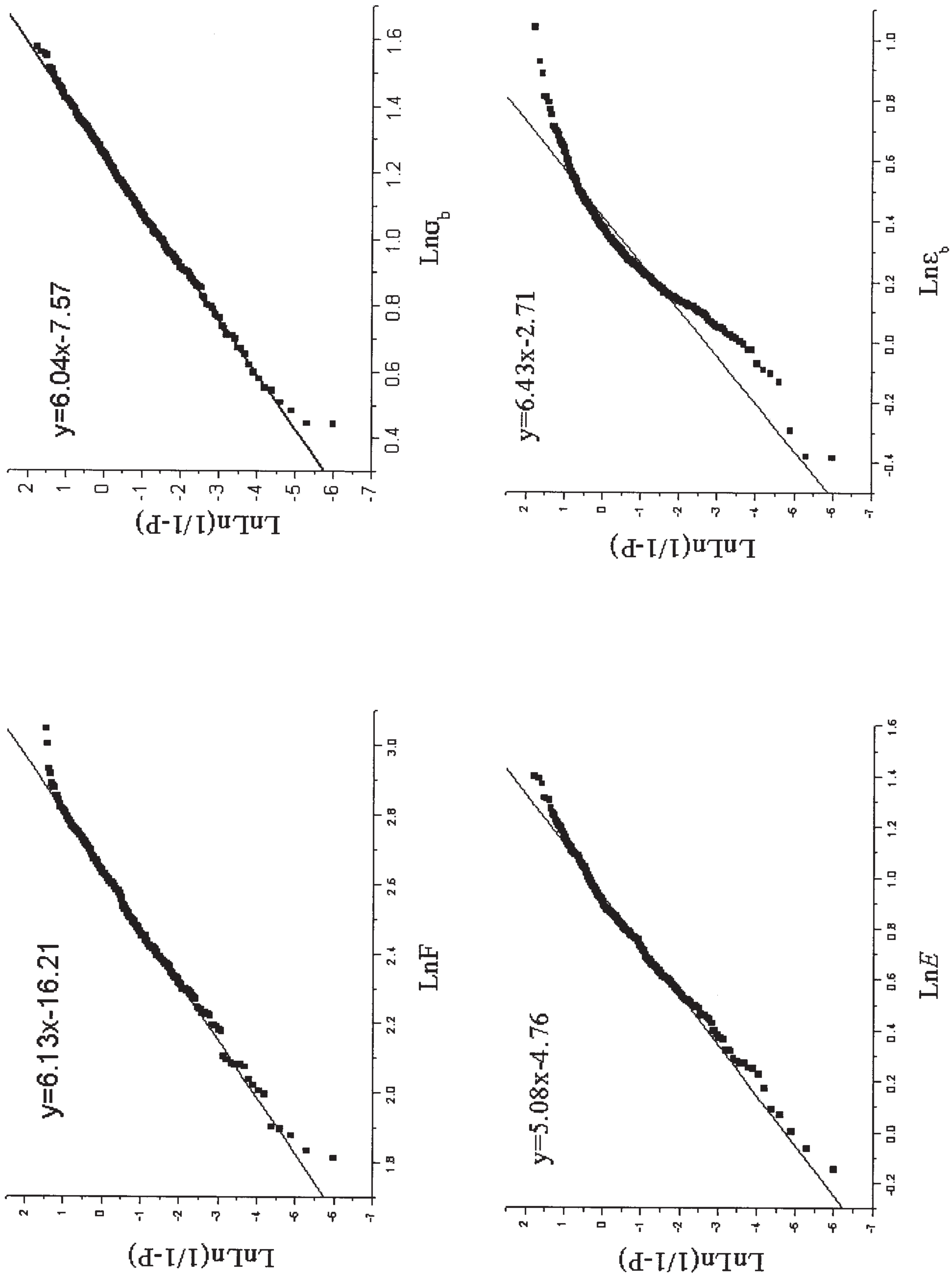

Figure 3 Weibull plots of the tensile parameters (number = 402).

TABLE II
Comparison of the Measured Data and the Parameters of the Weibull Distribution

Parameter	CV_{0m}(%)	m	χ_{0m}	χ_0	Δ (%)
F	18.84	6.23	13.90	13.90	0
σ	19.37	6.04	3.49	3.51	0.57
E	23.36	5.08	244.68	248.08	1.39
ε	19.52	6.39	1.46	1.52	4.11

of Weibull plots, but the strain distribution should be of a Weibull distribution theoretically.

If the stress and modulus are both of a Weibull distribution, their failure probabilities are the following: $P_{\text{stress}} = 1 - \exp[-(\sigma/\sigma_0)^{m^\sigma}]$ and $P_{\text{modulus}} = 1 - \exp[-(E/E_0)^{m^E}]$. Therefore, their survive probabilities are $S_{\text{stress}} = \exp[-(\sigma/\sigma_0)^{m^\sigma}]$ and $S_{\text{modulus}} = \exp[-(E/E_0)^{m^E}]$. Because strain ε is equal to σ/E, the survive probability of the strain is $S_{\text{strain}} = S_{\text{stress}}/S_{\text{modulus}} = \exp[(\varepsilon/E_0)^{m^E} - (\varepsilon/\sigma_0)^{m^\sigma}]$. Then, the failure probability of the strain is $P_{\text{strain}} = 1 - \exp[(\varepsilon/E_0)^{m^E} - (\varepsilon/\sigma_0)^{m^\sigma}]$. As we can see in Figure 5, the strain distribution fits well with $1 - \exp[(\varepsilon/1.07)^{3.02} - (\varepsilon/1.05)^{3.85}]$. Therefore, the strain distribution is still thought to be of a Weibull distribution, perhaps just a higher order Weibull distribution, or there might be testing error in the strain measurement.

Difference between the stress and force distributions of the carbon fibers

Figure 3 shows that the value of the shape parameter obtained from the force distribution is larger than that of the stress distribution; this means that the variation of the stress distribution is wider than that of the force distribution. If all the samples were of the same diameter, the force distribution should be the same as the stress distribution. The difference between the force distribution and stress distribution is caused only by the fiber diameter and its variation. To show the relationship of the force, stress, and diameter clearly, all the samples have been divided into eight groups according to their fineness, and the curves for the force–diameter and stress–diameter relationships are drawn in Figure 6. The maximal, average, and minimal strength and force values of the carbon fibers in the eight groups illustrate that there is no obvious relationship between the force and diameter, whereas the mean stress of the carbon fiber decreases clearly as the diameter increases. This results from the volume dependence.

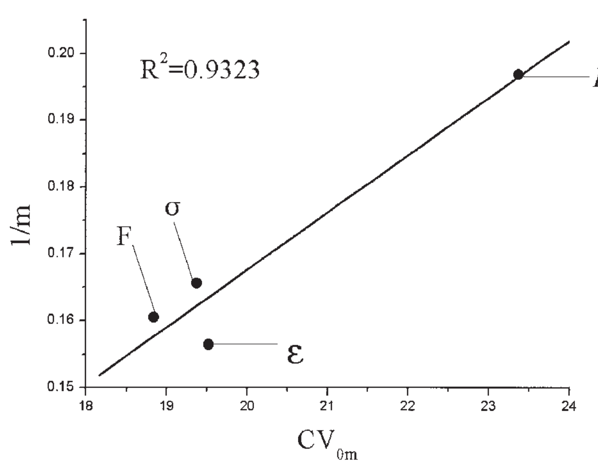

Figure 4 Linear fit for $1/m$ and CV_{0m}.

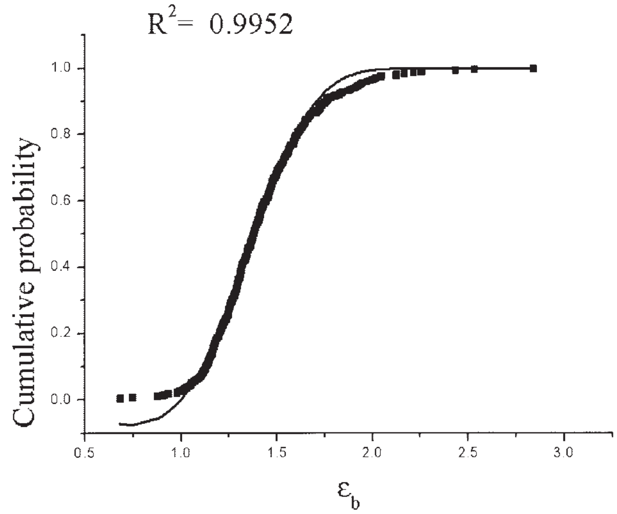

Figure 5 Weibull distribution for the strain (number = 402).

Variation of the sample size and volume dependence

The Weibull distribution is based on the assumption that the strength of carbon fibers decreases with their volume because it is more likely to find flaws of a critical size in large components than in small ones. Spencer[8] proposed the term *fracture zone*. He thought that the breaking of a specimen occurs at a fracture zone, so that the longer the gauge length is or the larger the sample diameter is, the larger the probability of encountering the weaker fracture zone is, and the lower the strength is. As shown in Figure 7, the linear relationship between the volume and strength exists only when the gauge length or the diameter is the same. A–C represent the volume–strength relationship of the samples with 15-, 30-, and 40-mm gauge lengths, respectively, and with the same mean diameter of 7.0 μm, and D stands for the mean-volume/mean-strength relationship of samples A–C.

Sample length effect

According to Peirce's weak-link theory,[9] the measured mean strength of fibers decreases as the test length is

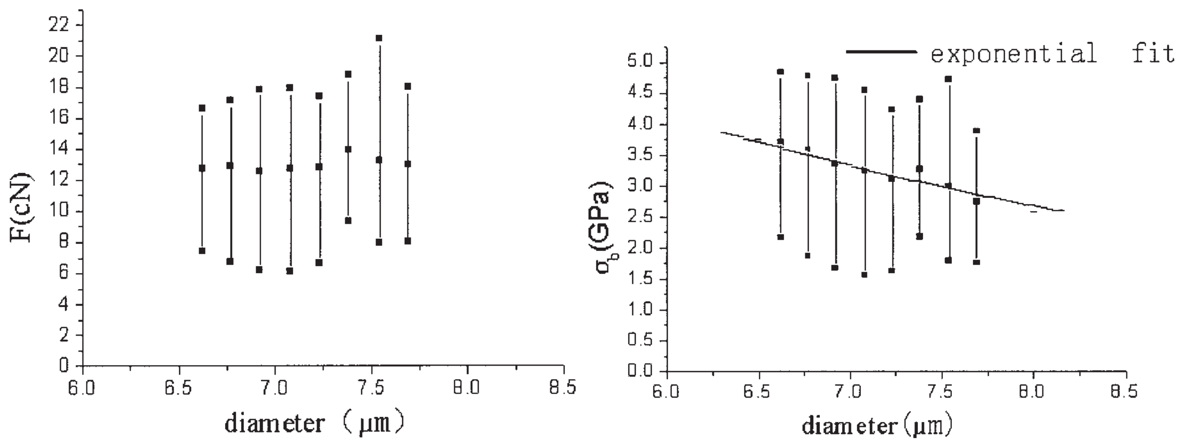

Figure 6 Strength variation of carbon fibers of different diameters.

increased. If a fiber is assumed to be modeled solely as a chain of *n*-link series, it will break at its weakest link. The fiber strength decreases with increasing specimen length because the probability of encountering a weaker link increases as the gauge length increases. The characteristic strengths of two samples of the same mean diameter but different lengths can be obtained as follows:

$$\sigma_{0(2)} = \sigma_{0(1)}\left(\frac{L_1}{L_2}\right)^{1/m} \tag{7}$$

where $\sigma_{0(2)}$ and$\sigma_{0(1)}$ are the characteristic strengths for lengths L_2 and L_1, respectively.

Usually, the diameter here is the minimum value along the fiber, whereas the length means the nominal gauge length. Equation (7) provides an excellent prediction of the fiber strength distributions at longer gauge lengths, but the extrapolation evaluation to very short gauge lengths yields a higher fiber strength than those measured. This indicates that the clamp effect or end effect is in function; that is, the failure of some fibers is due to the stress concentrations at each adhered end.[10,11] Besides the end effect, the ineffective adhesion length and *OO′* have an affect on the actual gauge length, too. Therefore, in eq. (7), *L* should be not the nominal gauge length but the actual gauge length, especially when the nominal gauge length is small.

As we can see in Figure 8, the slope of the gauge-length effect is close to that of D in Figure 7 because the mean diameter of samples A–C in Figure 7 is close.

Sample diameter effect

In Knox and Whitwell's theory,[12] a fiber is considered to be composed of *n*-element chains, which are assumed to be in parallel and have uniformly distributed strength. The fiber will survive when *m* of the *n* elements still work. The fiber strength decreases with increasing specimen diameter because the probability of encountering a group of severer flaws that make

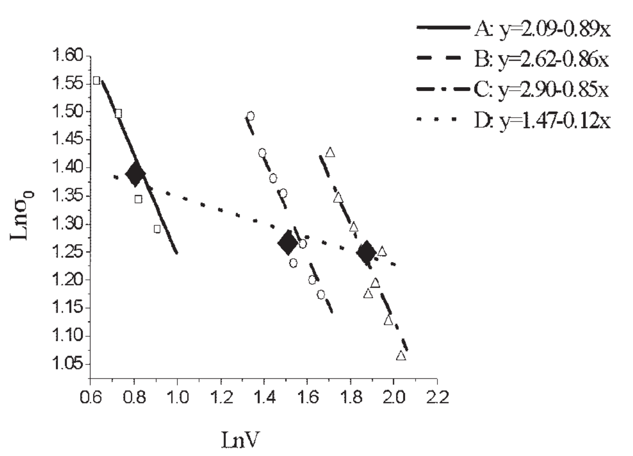

Figure 7 Dependence of the tensile strength on the fiber volume (number = 801).

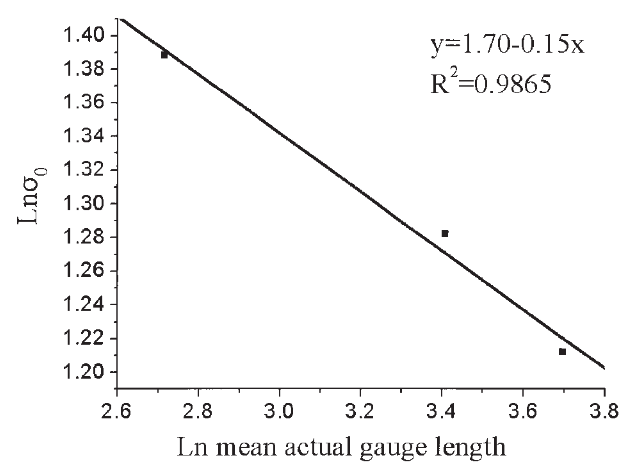

Figure 8 Dependence of the tensile strength on the gauge length (number = 402).

more than $n - m$ elements out of work increases as the area of the cross section increases.

The volume dependence of the strength was observed not only in the axial direction but also in the radial direction of the fiber. In these experiments, as shown in Figure 9, the gauge length was 40 mm. The slope of the gauge-length effect is close to half of that of A–C in Figure 7, and the difference is caused by the gauge-length variation, which is not considered here because it is very limited. From Figure 9, a value for the slope of -1.82 has been obtained, which is much smaller than that obtained from the dependence of the tensile strength on the gauge length (-0.12 in Fig. 7 and -0.15 in Fig. 8). This indicates that the size dependence of the strength in the radial direction is much stronger than that in the axial direction.

Effect of the sample volume on the stress distribution

When the volumes of the samples are not considered constant, the Weibull distribution can be described as follows:

$$P(V,\sigma) = 1 - \exp\left\{-\left(\frac{V}{V_0}\right)\times\left[\frac{\sigma}{\sigma_0}\right]^m\right\} \tag{8}$$

where V is the volume and V_0 is the mean volume. Because of the variation of the gauge length and diameter, the volume of the samples cannot be regarded as the same. In this experiment, when the gauge lengths are the same, the biggest fiber is 68% bigger in volume than the smallest fiber. Therefore, it is not advisable to consider the volume of all samples as an average constant, although the same gauge length is set. For further explanation, the Weibull plot was obtained from eq. (8), and V_0 here is $\bar{V}$ to normalize V/V_0. Compared with the m value calculated from

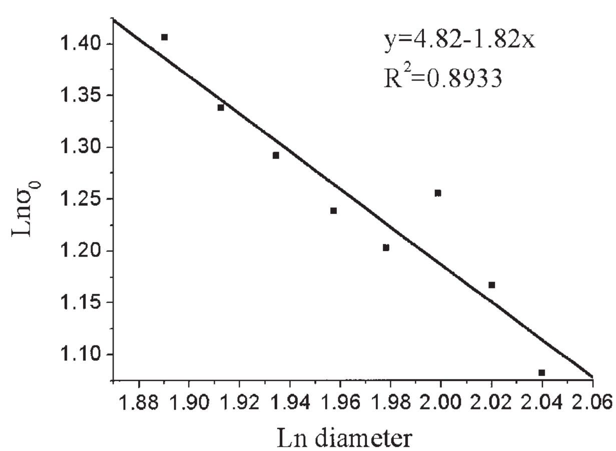

Figure 9 Dependence of the tensile strength on the fiber diameter (number = 402).

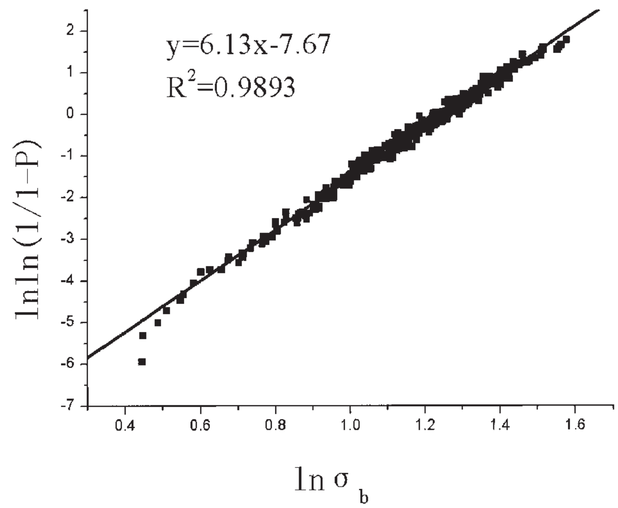

Figure 10 Weibull plot with volume variation.

Figure 3 ($m = 6.04$), the value of m (6.13) obtained from Figure 10 is a little larger. This means that (1) the stress variation obtained in this experiment was induced partly by the volume variation, (2) the main reason for the variation was the effect of FWLs (which will be introduced in part III of this series), and (3) the variation of the sample volume was the only factor for the difference between the shape parameters obtained from Figure 3 and 10.

CONCLUSIONS

Although force and stress can both be fitted to a Weibull distribution, the variation of the stress distribution is wider than that of the force distribution. Therefore, the stress of carbon fibers cannot be obtained by the division of the force by the mean cross section of all the fibers directly because the force is related not only to the stress itself but also to the diameter.

The volume dependence of the carbon fiber (with both the length and diameter effects included) has been analyzed. With the same diameter but different gauge lengths, the volume effect depends on the gauge length or, more accurately, on the actual gauge length. With the same gauge length but different diameters, the volume effect relies on the diameter. In general, the volume dependence in the radial direction is much larger than that in the axial direction of the fiber. To understand the effect of flaws on the tensile strength, the effect of the volume variation on the stress variation must be considered, especially for a large diameter variation ($CV_D > 3.5\%$).

Carbon fibers are brittle and exhibit a large amount of scatter in their tensile properties. Sample preparation and tensile testing for these fibers are difficult and prone to fiber damage. Therefore, it is necessary to prepare single-fiber samples carefully and to do a large number of fiber tensile tests to avoid various operating and systematic errors (which will be discussed in part II) and achieve successful and accurate measurements.

References

1. Jones, J. B.; Barr, J. B.; Smith, R. J Mater Sci 1980, 15, 2455.
2. Chi, Z.; Chou, T. W.; Shen, G. J Mater Sci 1984, 19, 3319.
3. Bennett, S. C.; Johnson, D. J. J Mater Sci 1983, 18, 3337.
4. Moreton, R. Fiber Sci Technol 1969, 1, 273.
5. Tetsuy, T.; Takashi, M. Mater Sci Eng A 1997, 238, 336.
6. Masson, J. J.; Schulte, K.; Girot, F.; Petitocorps, Y. L. Mater Sci Eng A 1991, 135, 59.
7. Pickering, K. L.; Murray, T. L. Compos A 1999, 30, 1017.
8. Spencer-Smith, J. L. J Text Inst 1947, 38, 257.
9. Peirce, F. T. J Text Inst T 1926, 17, 355.
10. Padgett, W. J.; Durham, S. D.; Mason, A. M. J Compos Mater 1995, 29, 1873.
11. Stoner, E. G.; Edie, D. D.; Durham, S. D. J Mater Sci 1994, 29, 6561.
12. Knox, L. J.; Whitwell, J. C. Text Res J 1971, 41, 510.