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Electrical resistivity of submicron-diameter carbon-filament compacts

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Abstract

The electrical resistivity of submicron-diameter carbon-filament compacts was decreased by increasing the filament diameter from 0.05 to 0.16 μm, and also by graphitization of the filaments. The use of nickel-coated carbon filaments gave even lower resistivity. The compacts exhibited lower resistivity than the corresponding polymer-matrix composites, such that the difference between compact and composite diminished with increasing filament volume fraction.

Keywords: A. Carbon composites; A. Carbon filaments; A. Catalytically grown carbon; D. Electrical properties; D. Transport properties.

1. Introduction

Submicron diameter carbon filaments are mainly those that are grown catalytically from carbonaceous gases at 500–700°C [1,2], although they include the carbon nanotubes [3], which typically have diameters in the nanometer range. Due to the higher yield in production, the former is more abundant than the latter and applications involving the former are more well developed than those involving the latter. Submicron carbon filaments are to be distinguished from conventional carbon fibers, which are made by pyrolysis of pitch or polymer [4–6]. They are also to be distinguished from vapor grown carbon fibers (VGCF), which are prepared by pyrolysis of carbonaceous gases to non-catalytically deposit carbon on catalytically grown submicron diameter carbon filaments at 950–1100°C [7–14]. Carbon filaments differ from both conventional and vapor grown carbon fibers in their small diameter. Conventional carbon fibers typically have a diameter around 10 μm and VGCF have diameters up to 10 μm. Both carbon filaments and VGCF are not continuous, though the latter can be longer than the former. In contrast, conventional carbon fibers can be continuous. In spite of the discontinuous nature of carbon filaments, the aspect ratio can be quite high, due to the small diameter. Carbon filaments tend to be not straight. Thus, they typically have a morphology that resembles cotton wool.

Carbon filaments are commercially available, though not in large volumes. As the amount of usage increases, the price of carbon filaments will fall. According to Applied Sciences Inc. (Cedarville, Ohio), which manufactures catalytically grown carbon filaments, the price will fall to U.S. $2–3 per pound. This price is even lower than that of short isotropic pitch based carbon fibers. In order for the usage to increase, applications must be developed.

Much research has been conducted to understand the process of catalytic growth of carbon filaments [1,2]. However, relatively little attention has been given to the applications of submicron diameter carbon filaments, although considerable progress has recently been made. These applications include structural applications, electromagnetic interference shielding, electromagnetic reflection, surface electrical conduction, DC electrical conduction, field emission, electrochemical applications, thermal conduction, strain sensors, porous carbons and catalyst support.

Many of the applications (particularly electromagnetic, electrical and strain sensor applications) involve the use of the carbon filaments in the form of a composite [14], particularly a polymer-matrix composite. This is because a composite provides a bulk form which is convenient to handle and shape. Other applications (particularly electrochemical, porous carbons and catalyst support applications) involve the use of the carbon filaments in the form of a

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compact, which is like a composite without a matrix. Without a matrix, the filaments can make direct contact with one another, in contrast to the presence of a matrix film at the junction of filaments when a matrix is present. The matrix is usually much less conducting electrically than the carbon filaments, so its presence increases the electrical resistance of the junction between filaments. Hence, the electrical resistivity of a compact is expected to be less than that of the corresponding composite with the same filament volume fraction. Thus, study of the compact is relevant to applications involving compacts as well as those involving composites. This paper is focused on the electrical resistivity of carbon filament compacts. Prior work has addressed the resistivity of carbon filament composites [15–17], but relatively little work has been done on the resistivity of carbon filament compacts [17,18].

2. Experimental methods

Carbon filament compacts were prepared by compacting the filaments (without a binder) in a steel mold via a steel piston. Controlled pressure was provided by a hydraulic press. By varying the pressure, the density (and thereby the filament volume fraction) of the compact was varied. The pressure caused some degree of preferred orientation of the filaments in the plane perpendicular to the pressure direction. However, the filaments were randomly oriented in this plane. The direction of electrical resistivity measurement was in this plane.

The electrical resistivity of carbon filament compacts was measured by using the four-probe method. The testing fixture was made of steel and is shown in Fig. 1. The design incorporates a rectangular cavity into which the carbon filaments were placed and compacted using a rectangular piston at a controlled pressure. Secured to the ends of the mold were probes (5 inches or 130 mm apart) used to pass current. Attached to the steel piston were two more probes placed at a known distance (1) apart. The potential developed across these two probes was measured as current was passed through the end probes. The compact electrical resistivity (ρ) was determined as a function of the distance between two inner probes, 1, the cross-sectional area of the sample, A, which is a function of the piston position, and the potential drop, ΔV, between the probes for a known current flow, I, through the compact, using the equation

$$\rho = (\Delta V/I)(A/1) \quad (1)$$

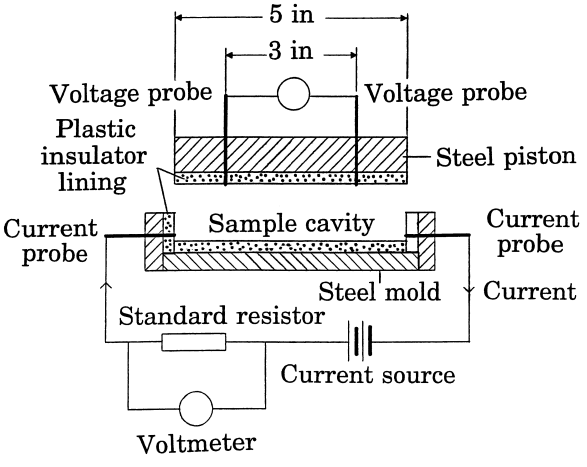

Fig. 1. Four-probe electrical resistivity measurement of a compact

The carbon filaments used were supplied by Applied Sciences, Inc. (Cedarville, Ohio, US). Two types of filaments were used. One is designated 'H'. The lot used in this work was lot 'H79'. The other is designated 'ADNH'. The lot used was 'ADNH-62'. Both types of filaments were made using methane as the primary source gas and an iron-containing catalyst. Hydrogen sulfide was added to the feedstock in small amounts to increase the filament yield. It has been reported that the sulfur addition causes the iron to melt and encourages filament growth by the vapor–liquid–solid process, as hydrocarbons adhere better to molten particles and carbon atoms may diffuse more rapidly through molten particles [19]. The H79 was grown without ammonia gas in the feedstock (in contrast to ADNH) and at a lower temperature compared to that used for ADNH.

To assess the impact of crystallinity on the electrical performance of the carbon filaments, the ADNH carbon filaments were graphitized at 2600°C. In this process, the filaments were placed on a graphite sagger and packed on all sides in graphitized charcoal to a depth of approximately one inch. The graphitized charcoal was then surrounded by an additional layer of ungraphitized charcoal. The self-generating atmosphere (produced by the volatization of the ungraphitized charcoal) protected the load from oxidation by air. Current was passed through the graphite sagger at a rate of 8 kW/lb, thus heating the load to the graphitization temperature after approximately 32 h. The load was held at the graphitization temperature for 10–12 h. The power was disconnected and the filaments were allowed to cool to room temperature – a slow process requiring 3 to 4 days. X-ray diffraction showed that graphitization caused the 002 graphite peak to be much more intense and sharp, indicating increased crystallinity.

The basic properties of carbon filaments, as provided by Applied Sciences Inc., are listed in Table 1. The surface area in Table 1 was calculated, according to R.L. Alig of Applied Sciences Inc., by assuming that the fiber is a solid cylinder with a density of 2 g/cm^3. This density was used to obtain the filament volume fraction from the density of a compact.

A filament is actually a microtube. The inner hole

Table 1
Properties of carbon filaments

	Type 'H'	Type 'ADNH'
Diameter (μm)	0.05	0.16
Surface area (m^2/g)	40	12.5
Bulk density (cm^3/g) (Compressed)	623	1620
Surface treatment	None	Nitrogen groups
Sizing	None	None
SEM morphology	Kinky mass	Entwined mass
Density (g/cm^3)	2	2
Aspect ratio	20–50	50–200

diameter of type ADNH, from Applied Sciences' limited SEM photographs, varies from approximately 20 to 75 nm. Because of its 'kinky' nature, the inner hole diameter of H type filaments is difficult to estimate.

3. Results and discussion

The compacting pressure is directly proportional to the contact pressure between filaments for a given filament geometry. It is well known that the contact resistivity decreases with increasing contact pressure for electrical contacts in general. Furthermore, the filament volume fraction increased as the compacting pressure increased. By increasing the pressure on the piston, the electrical resistivity decreased and gradually leveled off, due to the leveling-off of both contact resistivity and filament volume fraction. At the same filament volume fraction (i.e., the same density of the compact), the resistivity of the compact decreases in the order: H79, ADNH (as received) and ADNH (graphitized), as shown in Table 2. For example, at a density of 0.47 g/cm^3, the compact resistivity is 0.23, 0.053 and 0.0095 Ωcm for H79, ADNH (as received) and ADNH (graphitized) respectively. It is believed that the higher electrical resistivity of the H79 filament compact is partly due to the smaller diameter of the filaments. The diameter ratio of ADNH to H79 is about 3.2, so their cross-sectional area ratio is about 10. This means that an H79 filament compact will have at least ten times as many contacts as an ADNH filament compact, therefore resulting in a compact of higher resistivity. Another reason is related to the thicker layer of the tarry material deposited during filament fabrication on the surface of H79 filaments [20]. The high resistivity of the H79 compact is also partly due to the high resistivity of the H79 filaments themselves, as shown by the analysis below. The low resistivity of the graphitized ADNH compact is due to the low resistivity of the graphitized ADNH filaments themselves, as shown by the analysis below.

Three models, which assume no contact resistance between filaments and no dead ends for the filaments, are used in this work to estimate the filament resistivity from the compact resistivity. The estimates correspond to the high conductivity limits.

A simple model is based on the Rule of Mixtures. If, in the compact, all filaments are straight and aligned in one direction, the compact conductivity in the filament direction can be expressed as

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \quad (2)$$

where σ_c is compact conductivity, σ_f is filament conductivity, and σ_m is matrix conductivity, V_f is filament volume fraction and V_m is the matrix volume fraction.

In this case, the matrix is air. Thus σ_m is assumed to be zero. Thus Eq. (2) can be written as

$$\sigma_c = \sigma_f V_f \quad (3)$$

or

$$\rho_f = \rho_c V_f , \quad (4)$$

where ρ_f is the filament resistivity and ρ_c is the compact resistivity.

Since this model assumes that all filaments are straight

Table 2
Electrical resistivity of carbon filament compacts at various pressures

Pressure (MPa)	Carbon filament (H79)		Carbon filament (ADNH, as received)		Carbon filament (ADNH, graphitized)	
	Resistivity (Ωcm)	Density (g/cm^3)	Resistivity (Ωcm)	Density (g/cm^3)	Resistivity (Ωcm)	Density (g/cm^3)
0.35	1.24	0.18	0.38	0.16	0.030	0.19
0.70	1.00	0.25	0.23	0.20	0.020	0.27
1.1	0.69	0.31	0.16	0.24	0.015	0.33
1.4	0.43	0.35	0.13	0.27	0.012	0.38
2.1	0.28	0.43	0.098	0.33	0.0095	0.47
2.8	0.21	0.49	0.078	0.37	0.0079	0.54
3.5	0.19	0.55	0.067	0.41	0.0069	0.60
4.9	0.14	0.66	0.053	0.47	0.0055	0.73
7.0	0.11	0.80	0.041	0.56	0.0042	0.90

and aligned in one direction, the σ_c is the highest possible value for a given σ_f. In other words, the ρ_f is the upper limit value for a given σ_c.

The second model used to estimate the compact conductivity assumes that the conducting medium comprises straight short fibers randomly distributed in three-dimensional space [7]. Assuming that the angle between the axis of any short fiber and the current direction is θ, the possibility for a fiber to be in a direction between θ and $\theta+\delta\theta$ in a three-dimensional space is $\sin\theta*(\delta\theta/2)$[1]. The effective material contributing to conduction is reduced by a factor of $\cos^2\theta$ because the conducting fiber is not parallel to the current direction. Thus, the geometric factor g can be calculated by the equation

$$\begin{aligned} g &= \frac{2}{\pi/2}\int_0^{\pi/2}\cos^2\theta\,\sin\theta\,\mathrm{d}\theta/2 \\ &= \frac{2}{\pi}\int_0^{\pi/2}\cos^2\theta\,\sin\theta\,\mathrm{d}\theta \\ &= \frac{2}{3\pi} \end{aligned} \tag{5}$$

Hence, equation $\sigma_c=\sigma_f V_f$ becomes

$$\sigma_c = \frac{2}{3\pi}\sigma_f V_f \quad \text{or} \tag{6}$$

$$\rho_f = \frac{2}{3\pi}\rho_c V_f \tag{7}$$

This three-dimensionally random distribution model is the other extreme compared to the Rule of Mixtures, which requires one-dimensional alignment of the conducting units. In this model, all the conducting units are randomly distributed in three-dimensional space and every conducting unit contributes to the conduction of the compact, such that there is no dead end for each unit electrically. Thus, σ_c is the lower limit for a given σ_f. In other words, ρ_f is the lower limit for a given σ_c.

In the experiments described above, the filaments were compressed by the piston to form a somewhat two-dimensionally aligned compact. Similarly, the possibility of a fiber layer to be oriented between θ and $\theta+\delta\theta$ in two-dimensional space is $\delta\theta/2\pi$[2]. A two-dimensional model could be derived by calculating the geometric factor g as

$$\begin{aligned} g &= \frac{4}{\pi/2}\int_0^{\pi/2}\cos^2\theta\,\mathrm{d}\theta/2\pi \\ &= \frac{4}{\pi^2}\int_0^{\pi/2}\cos^2\theta\,\mathrm{d}\theta \\ &= 1/\pi \end{aligned} \tag{8}$$

Thus, equation $\sigma_c=\sigma_f V_f$ now becomes

$$\sigma_c = \frac{1}{\pi}\sigma_f V_f \tag{9}$$

or

$$\rho_f = \frac{1}{\pi}\rho_c V_f \tag{10}$$

Eqs. (9) and (10) constitute a better approach to modeling the consequence of the compacting experimental method and therefore are more accurate than either Eqs. (4) or (7). In reality, however, the fibers in the compact are not in a perfectly two-dimensional configuration, so the actual resistivity of a single fiber should be lower than that calculated by using Eq. (10), i.e., between the values obtained by using Eqs. (7) and (10), and depends on the real configuration.

The measured electrical resistivities of carbon filament compacts are summarized in Table 2. The H79 filaments exhibited higher electrical resistivity than the ADNH filaments, both as received. Graphitization reduced the resistivity of the ADNH filaments, as expected.

Estimated filament resistivity values obtained by using the three models are listed in Table 3. The compact electrical resistivity values listed in Table 3 are values obtained at a 7 MPa compacting pressure and the filament volume fractions were calculated by using the density values of Table 2 at the same pressure. The estimated resistivity of the graphitized ADNH filament itself is 0.0005 Ωcm (between the values obtained by the second and third models), which is much higher than those of metals.

The graphitization of ADNH carbon filaments causes the

[1] The volume δV from θ to $\theta+\delta\theta$ of unit length fiber is

$$\begin{aligned} \delta V &= 2\pi\int_0^1\int_\theta^{\theta+\delta\theta} r^2\sin\varphi\,\mathrm{d}r\,\mathrm{d}\varphi \\ &= \frac{2\pi}{3}[\cos\theta-\cos(\theta+\delta\theta)] \\ &= \frac{2\pi}{3}[\cos\theta-(\cos\theta\cos\delta\theta-\sin\theta\sin\delta\theta)] \end{aligned}$$

Since $\delta\theta$ is very small, $\cos\delta\theta\sim1$ and $\sin\delta\theta\sim\delta\theta$. Thus, $\delta V\sim(2\pi/3)\delta\theta\sin\theta$. Under the assumption of uniform distribution, the probability is proportional to the volume, so that

$$P=\frac{\delta V}{V}=\frac{\frac{2\pi}{3}\delta\theta\sin\theta}{\frac{4\pi}{3}}=\frac{1}{2}\delta\theta\sin\theta.$$

[2] The area δS from θ to $\theta+\delta\theta$ of unit length of fiber is $\delta S=\delta\theta/2$. Thus, the probability becomes $P=\delta S/S=\delta\theta/2\pi$.

Table 3
Electrical resistivity of carbon filaments (ρ_f) estimated from compact's resistivity (ρ_c) by using three models

Filament type	ρ_c (Ωcm)	V_f	$\rho_f = \rho_c V_f$ (Ωcm)	$\rho_f = \frac{1}{\pi} \rho_c V_f$ (Ωcm)	$\rho_f = \frac{2}{3\pi} \rho_c V_f$ (Ωcm)
H79, as received	0.106	0.398	0.0421	0.0134	0.0089
ADNH, as received	0.041	0.281	0.0115	0.0037	0.0024
ADNH, graphitized	0.0042	0.452	0.0019	0.0006	0.0004

resistivity of the compact with 14 vol.% carbon filaments to decrease from 0.12 to 0.019 Ωcm (Table 2). A compact with 0.4-μm diameter nickel filaments (obtained by electroplating the ADNH carbon filaments by nickel) at the same volume fraction exhibits a resistivity of 0.00014 Ωcm [17]. Hence, graphitization is not as effective as nickel coating in lowering the resistivity, as expected from the metallic nature of nickel.

Comparison of the electrical resistivity of carbon filament (ADNH, as received) compacts of this work and that of corresponding (also ADNH) polymer-matrix composites [17] shows that the compact exhibits lower resistivity than the composite with the same filament volume fraction. For example, at 10 vol.% filaments, the resistivity is 0.23 and 2 Ωcm for compact and composite respectively; at 16.5 vol.% filaments, the resistivity is 0.1 and 0.2 Ωcm for compact and composite respectively; at 28 vol.% filaments, the resistivity is 0.04 Ωcm for both compact and composite. Hence, the difference in resistivity between compact and composite diminishes as the filament volume fraction increases. This is due to the decrease in thickness of the polymer matrix film at the junction of filaments as the filament volume fraction in the composite increases, and the increase in the contact resistivity of the junction as the matrix film becomes thicker.

Based on geometric considerations, it is commonly assumed that, at the same filament volume fraction, filaments of a smaller diameter would give a composite with a lower resistivity, when the filaments are more conducting than the matrix. This work shows that this assumption is not always valid, as the H79 filaments compact exhibits a higher resistivity than the ADNH (as received) filament compact at the same filament volume fraction.

4. Conclusion

The electrical resistivity of submicron-diameter carbon-filament compacts was higher for filaments of 0.05 μm diameter than for filaments of 0.16 μm diameter at the same filament volume fraction. The compact's resistivity was decreased by graphitization of the filaments, though the use of nickel-coated carbon filaments (not graphitized) gave compacts of even lower resistivity. Corresponding polymer-matrix composites exhibited higher resistivity than the compacts, though the difference between corresponding compact and composite diminished as the filament volume fraction increased. The lowest resistivity attained in carbon filament (without nickel coating) compacts was 0.004 Ωcm; this corresponds to an estimated filament resistivity of around 0.0005 Ωcm.

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