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LETTERS TO THE EDITOR

Piezoresistive behavior of carbon fiber in epoxy

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The resistive and piezoresistive behaviors of carbon fibers are relevant to the potential use of carbon fibers as a strain/stress sensor in a smart composite structure. The resistive behavior pertains to the reversible increase of the electrical resistance (not resistivity) of a fiber upon tensile strain, as previously observed for a bare low-modulus carbon fiber (including the fiber of this work) and shown to be mainly due to dimensional change rather than resistivity change [1-6]. The piezoresistive behavior pertains to the reversible change in the electrical resistivity upon strain, as reported here. As carbon fibers are commonly used in a polymer (e.g. epoxy) matrix rather than being bare, the electromechanical (whether resistive or piezoresistive) behavior of a carbon fiber in a polymer matrix needs to be studied before the fiber can be used as a sensor in a polymer-matrix composite. This paper extends our previous work on a bare carbon fiber [6] to the case of a carbon fiber embedded in epoxy. It has been reported that a carbon fiber in epoxy increases its electrical resistivity during the curing of the epoxy due to the residual compressive stress resulting from the shrinkage during curing and thermal contraction during cooling of the epoxy [5]. Since the residual compressive stress in the fiber is expected to decrease upon subsequent tension of the fiber, this observation suggests that the electromechanical behavior of a carbon fiber in epoxy may be different from that of a bare carbon fiber. However, [5] reported the same electromechanical behavior for bare carbon fiber and carbon fiber in epoxy. As the residual compressive stress in a fiber increases with increasing curing temperature [5], a higher curing temperature than used in [5] was used in this work. Consequently, the fiber resistivity (also resistance) increased by 10% after curing of epoxy in this work, whereas the fiber resistance increased by only 0.5% after room temperature curing in [5]. Thus, upon subsequent tension of the fiber in cured epoxy, we observed a decrease of the fiber resistance due to reduction of the residual compressive stress, whereas [5] observed an increase of the fiber resistance (as in the case of the bare fiber). Hence, a new electromechanical effect was observed in this work. This effect is a piezoresistive effect in which the resistivity of a carbon fiber in cured epoxy decreases reversibly upon tension of the fiber.

The carbon fiber used was 10E-Torayca T-300 (unsized, PAN-based), of diameter 7 μm, density 1.76 g/cm^3, tensile modulus 221 ± 4 GPa, tensile strength 3.1 ± 0.2 GPa and ultimate elongation 1.4%. The electrical resistivity was (2.2 ± 0.5) x 10^{-3} Ω.cm, as measured by the four-probe method using silver paint electrical contacts on single fibers. The epoxy used was EPON(R) resin 9405 together with curing agent 9470, both from Shell Chemical Co., in weight ratio 70:30. The recommended curing temperature is 150-180°C for this epoxy.

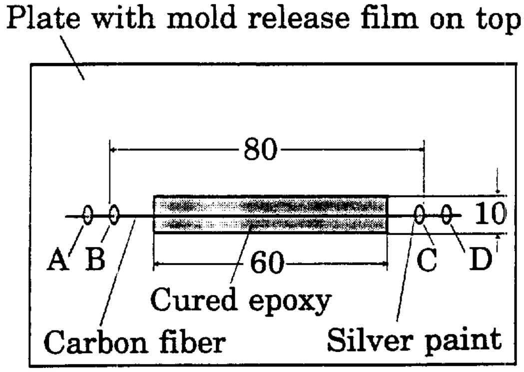

Fig. 1. Sketch of the resistance measurement set-up for single carbon fiber embedded in epoxy. A, B, C and D are four probes. A and D are for passing current; B and C are for voltage measurement. Dimensions are in mm.

The electrical resistance of a carbon fiber embedded in epoxy before and after the curing of the epoxy (at 180°C, without pressure, for 2 h), as well as during subsequent tensile loading, was measured using the sample configuration of Fig. 1. A single fiber was embedded in epoxy for a length of 60 mm and an epoxy coating thickness of 5 mm, such that both ends of the fiber protruded and were bare in order to allow electrical contacts to be made on the fiber using silver paint. Four contacts (labeled A, B, C and D in Fig. 1) were made. The outer two contacts (A and D) were for passing a current, whereas the inner two contacts (B and C, 80 mm apart) were for measuring the voltage. A Keithley 2001 multimeter was used for DC electrical measurements. The same electrical contact design was used in the authors' earlier work on the electromechanical behavior of a bare single carbon fiber (same fiber as used in this work).

Table 1. Electrical resistivity of carbon fiber before and after epoxy curing.

Resistivity before curing (10^{-3} Ω.cm)	Resistivity after curing (10^{-3} Ω.cm)	Fractional change in resistivity
2.24	2.46	9.8%
2.43	2.69	10.5%
2.17	2.39	10.2%
2.11	2.34	11.0%
2.58	2.83	9.6%
2.36	2.61	10.7%

Table 1 shows the electrical resistivity of carbon fiber before curing of epoxy and after both curing and subsequent cooling. Data for six samples are consistent, indicating that the resistivity of fiber increased by ~ 10% after curing and subsequent cooling. The fractional resistance increase was also ~ 10%.

It is known that the disparate thermal expansion properties of carbon fiber and epoxy lead to an inevitable build-up of residual thermal stress during the matrix (epoxy) solidification and subsequent cooling. Here we only consider the residual stress along the fiber direction (one dimension). Since the strain of matrix and fiber is the same (if adhesion is perfect),

$$\frac{\sigma_f}{E_f} + \alpha_f \Delta T = \frac{\sigma_m}{E_m} + \alpha_m \Delta T \qquad (1)$$

where

σ_f is the longitudinal residual stress built up in the fiber,
σ_m is the residual stress built up in the matrix,
E_f is the modulus of the fiber,
E_m is the modulus of the matrix,
α_f is the coeff. of thermal expansion of fiber,
α_m is the coeff. of thermal expansion of matrix, and
ΔT is the temperature change.

Since there is no external force on the specimen,

$$\sigma_f V_f + \sigma_m V_m = 0 \qquad (2)$$

where

V_f is the volume fraction of fiber, and
V_m is the volume fraction of matrix.

Combining equations (1) and (2), we have the following equation for calculating the residual stress in the fiber.

$$\sigma_f = \frac{E_f E_m V_m (\alpha_m - \alpha_f) \Delta T}{(V_m E_m + V_f E_f)} \qquad (3)$$

In this work, E_f = 221 GPa, E_m = 3.7 GPa, $\alpha_m = 42 \times 10^{-6}$ K^{-1}, $\alpha_f = 0.09 \times 10^{-6}$ K^{-1} and ΔT = 155 K. From equation (3), the residual thermal stress built up in the fiber reaches 1438 MPa. In this case of a single fiber in epoxy, the high residual stress is built up during curing and subsequent cooling. The observed resistance increase after curing and cooling is attributed to this residual stress.

Electromechanical testing of a single fiber in cured epoxy was conducted using the configuration of Fig. 1 during tension under load control, as provided by a screw-type mechanical testing system (Sintech 2/D). The crosshead speed was 0.1 mm/min. The strain was obtained from the crosshead displacement.

Fig. 2 shows the fractional change in resistance ($\Delta R/R_0$) of fiber in cured epoxy upon static tension up to fiber fracture. Due to the small strains involved, $\Delta R/R_0$ was essentially equal to the fractional change in resistivity. The $\Delta R/R_0$ decreased by up to ~10% upon tension to a strain of ~ 0.5% (a stress of 1320 MPa) and then increased upon further tension. The magnitude of resistance decrease of carbon fiber in initial tension is close to the value of the prior resistance increase during curing and cooling of epoxy. The stress at which the resistance decrease was complete (1320 MPa) is close to the value of 1438 MPa obtained from equation (3). Therefore, the initial decrease in $\Delta R/R_0$ in Fig. 2 is attributed to the reduction of the residual compressive stress in the fiber. The later increase in $\Delta R/R_0$ in Fig. 2 is attributed to damage in the fiber. Previous work on the electromechanical behavior of a bare carbon fiber had shown that damage causes the resistivity of the fiber to increase [6].

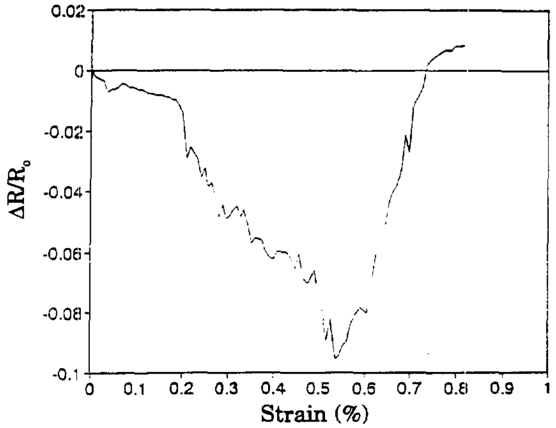

Fig. 2. The fractional electrical resistance change of single carbon fiber in epoxy under tension.

Fig. 3 shows the $\Delta R/R_0$ of fiber in cured epoxy upon tensile loading to a strain of ~ 0.3% and upon subsequent unloading. The $\Delta R/R_0$ decreased upon loading and increased back to the initial value upon unloading, indicating the reversibility of the electromechanical effect.

The $\Delta R/R_0$ per unit strain for the electromechanical effect of Fig. 3 is -17 (negative since $\Delta R/R_0$

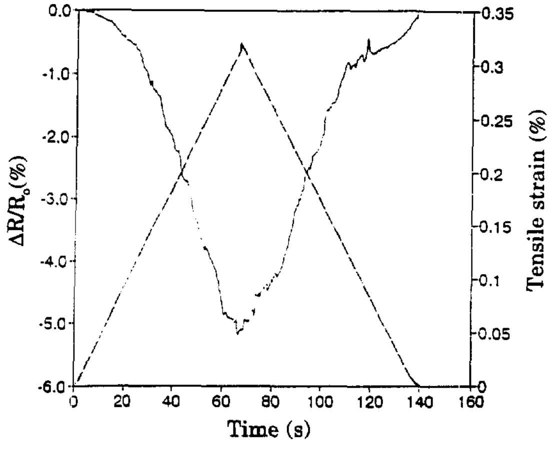

Fig. 3. Plots of $\Delta R/R_0$ vs. time and strain vs. time during tensile loading and unloading for single carbon fiber embedded in epoxy. Solid curve: $\Delta R/R_0$ vs. time. Dashed curve: tensile strain vs. time.

is negative). In contrast, $\Delta R/R_0$ per unit strain for the electromechanical effect associated with a bare carbon fiber and due to dimensional changes is 2 (positive since $\Delta R/R_0$ is positive). The large magnitude of $\Delta R/R_0$ per unit strain (called strain sensitivity or gage factor) for the new electromechanical effect of this paper makes this effect technologically attractive for use of a carbon fiber polymer-matrix composite as a strain sensor [7]. Indeed, the resistivity of a unidirectional epoxy-matrix composite (with the same fibers as used in this work, in the amount of 58 vol.%) in the fiber direction was observed to decrease reversibly upon tension of the composite in the fiber direction [7].

In conclusion, a new reversible electromechanical effect was observed in a single carbon fiber embedded in epoxy. It is a piezoresistive effect in which the resistivity of the fiber decreases reversibly upon tension of the fiber. It is attributed to the reduction of the residual compressive stress in the fiber. This effect provides a method for measuring the residual stress along the fiber direction. The value thus obtained for carbon fiber in epoxy is 1320 MPa. The residual stress is due to the shrinkage of the epoxy during cooling after curing. The effect is opposite to that of the corresponding bare carbon fiber (tested electromechanically using the same method as in this work), which reversibly increases in resistance (not resistivity) upon tension due to dimensional changes [6].

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A spectroscopic study on benzene soluble fraction from naphthalene pitch

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Carbons prepared at lower temperatures than 1000°C consist of discrete aromatic molecules [1], and hence these materials are considered to be included in a category of organic semiconductors. The authors have been interested in the development of electronically functional carbons by utilizing the semiconductive nature of these materials. The properties targeted are conductivity [2], photoconductivity [3,4], electrocatalytic activity [5] and sensing abilities for chemicals. When these materials are used for some electronic uses such as solar cell or photodetector, the favourable form of the substance for these purposes would be thin films. Vacuum evaporation [6], chemical vapour deposition [7] or plasma decomposition of hydrocarbon gases [3,4] are usually used to obtain thin films. The authors recently proposed an idea of utilizing extracts from a petroleum pitch as a candidate for the soluble carbonaceous materials [8]. Those extracts were successfully proved to give thin films by a spin coating technique, and the films thus coated on n-type silicon substrates, i. e. junctions between the extracts and n-Si, showed a photovoltaic effect toward near-infrared light. Further, the photocarrier generation was inferred to take place near the junctions of the diodes.

The mechanism of photocarrier generation in carbonaceous materials is believed to include the formation of electron-hole pairs, whose fate is to be separated by the action of electric field to become carriers responsible for current. If an electron acceptor or a donor is present near the photon absorber, i. e. aromatic molecules in carbonaceous materials, it will decrease the probability of recombination between the excited pairs of electrons and holes. It should be noted that the utilization of soluble carbonaceous materials, such as extracts from pitches, allows the addition of electronic active molecules. This should be an advantage of using the extracts for preparing thin film devices.

The aim of this study is to investigate the effect of the addition of an electron acceptor, bromanil (BA, see Fig. 1), to a benzene soluble fraction of a naphthalene pitch from the viewpoints of absorption and fluorescence spectroscopies.

The benzene soluble fraction used here was extracted from a naphthalene pitch provided by Professors I. Mochida and Y. Korai of Kyushu University, Japan, using a Soxhlet extractor at 110°C for 74 h. The soluble part (BS) was separated by filtration

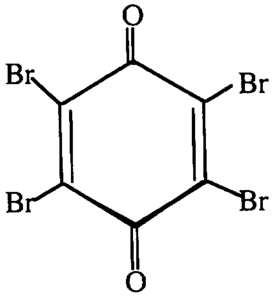

Fig. 1. Structure of bromanil.

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