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Carbon fiber mats as resistive heating elements

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Continuous carbon fibers are widely used as reinforcement in lightweight structural composite materials, particularly polymer–matrix composites. A less expensive form of carbon fiber is short (discontinuous) fibers, which can be made into a porous mat by the use of a small amount of an organic binder. The fibers in a mat are usually randomly oriented in two dimensions. They are made by wet-forming, as in papermaking. Applications of carbon fiber mats include electromagnetic interference (EMI) shielding [1,2], lightning protection [2], electrical grounding, fuel cell electrodes, composite reinforcement [3,4] and deicing (i.e. using the mat as a resistance heating element [5], which can be incorporated in or on a structural composite). As many of these applications benefit from a high electrical conductivity, metal coated carbon fibers are often used for mats. A common metal for this purpose is nickel [2], due to its resistance to oxidation and corrosion.

Graphite has long been used as a heating element. In addition to graphite in monolithic form [6], pyrolytic graphite deposited on boron nitride has been used [7]. Furthermore, polymer–matrix composites containing carbon fibers [8] or carbon black [9], and carbon–matrix composites [10] have been used. Flexibility or shape conformability of the heating element is desirable for many applications, such as the deicing of aircraft [11,12] and the heating of floors, pipes and boilers. Carbon fiber mat is thus attractive. It is also attractive because it is in a sheet form, is corrosion resistant, and can be incorporated in a structural composite. In contrast, conventional graphite requires expensive machining to attain the shape required for the heating element. This paper evaluates the effectiveness of carbon fiber mats as heating elements. Although their use as heating elements has been briefly reported [5], evaluation of their effectiveness has received little attention.

This paper addresses a carbon fiber mat with bare fibers (no metal coating) and one with metal (Ni–Cu–Ni) coated fibers. The trilayer (Ni–Cu–Ni) form of the coating is a technologically common form which takes advantage of the low electrical resistivity of copper and the superior oxidation resistance of nickel.

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The carbon fiber mats were nonwoven and kindly provided by Technical Fibre Products (Newburgh, NY, USA). The carbon fibers were PAN-based. The fiber diameter was 10 μm. The mat with bare carbon fibers contained 50% 1/2 inch (13 mm) fibers and 50% 1/4 inch (6.4 mm) fibers. The mat with metal-coated carbon fibers contained 100% 6 mm fibers. Both mats also contained a binder in the amount of 10 wt.%. The binder was poly-(vinyl alcohol) in case of bare fibers and was a crosslinked polyester in case of metal-coated fibers. The areal weight was 10 and 12 g/m^2 for bare and metal-coated fiber mats, respectively. The thickness was 150 and 210 μm for bare and metal-coated fiber mats, respectively, as measured in this work by optical microscopy.

Evaluation of a fiber mat as a heating element was conducted by passing a DC current (0.1–0.4 A) along the length of the specimen (100×10 mm in size) by using electrical contacts (80 mm apart and symmetrically located with respect to the mid-point of the length of the specimen) in the form of silver paint in conjunction with copper wire. The voltage drop (up to 17.1 and 7.4 V for bare and metal-coated fiber mats, respectively) along the length of the specimen was measured by using two other electrical contacts (60 mm apart and symmetrically located with respect to the mid-point of the length of the specimen), also in the form of silver paint in conjunction with copper wire. During the test, a weight (corresponding to a stress of 0.83 kPa) was applied to the top surface of the specimen in order to provide electrical contacts in the form of pressure contacts, since the silver paint degraded and diminished its adhesive ability as the specimen became hot. The weight was electrically insulated from the specimen, which was placed on a refractory brick. Room temperature was 19 °C. The temperature of the specimen was measured as a function of time during constant current application and in the subsequent period in which the current was off by using a K-type thermocouple located in the middle of the top surface of the specimen. The constant current period was long enough for the temperature to essentially level off to a maximum.

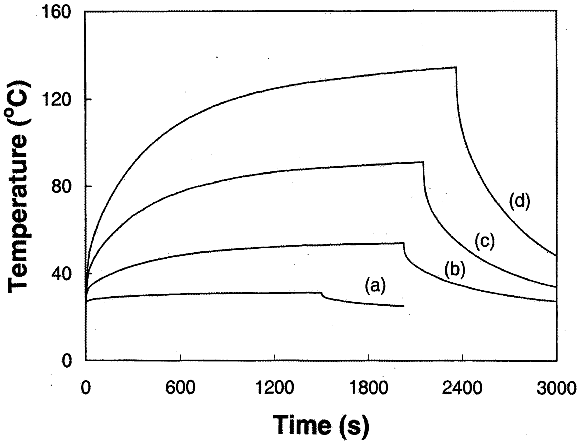

Fig. 1. Temperature variation during heating (current on) and subsequent cooling (current off) for mat with bare carbon fibers. The current was turned off at the time corresponding to the start of the temperature drop. (a), (b), (c) and (d) are for four power levels as shown in Table 1.

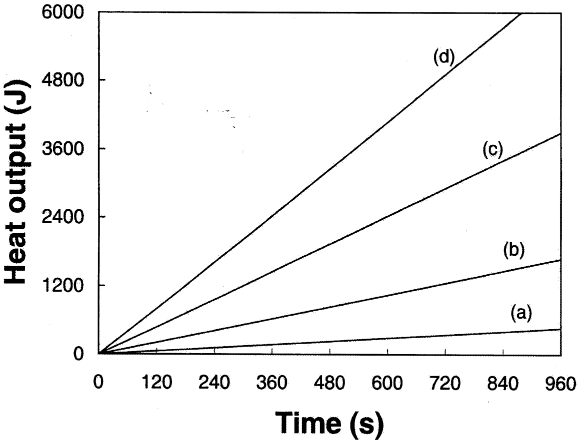

Fig. 2. Heat energy output vs. time during heating of mat with bare carbon fibers. (a), (b), (c) and (d) are for four power levels as shown in Table 1.

The volume electrical resistivity of each type of fiber mat in the plane of the mat was measured by using the four-probe method [13]. The outer contacts (80 mm apart) were for passing current while the inner contacts (60 mm apart) were for voltage measurement, as in the configuration for evaluation of the mat as a heating element. A Keithley multimeter was used for resistance measurement.

The thermal stability of the bare fiber mat was investigated by thermogravimetric analysis, using a Perkin-Elmer TGA7 system. The specimen (3.163 mg before heating) was heated in air from 30 to 250 °C at 5 °C/min.

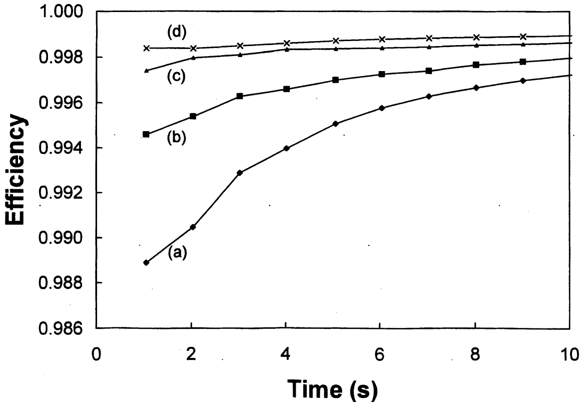

Fig. 3. Efficiency vs. time during heating of mat with bare carbon fibers. (a), (b), (c) and (d) are for four power levels as shown in Table 1.

Table 1
Effectiveness of carbon fiber mats for resistance heating; the initial temperature before heating was 19 °C (room temperature)

Fiber type	Designation	Current (A)	Voltage (V)	Electrical power input in the first 5 s (W)	Maximum temperature (°C)	Time to reach maximum temperature (s)	Time to reach half of the maximum temperature rise during heating (s)	Time to drop to half of the maximum temperature rise during cooling (s)	Temperature rise in the first 5 s (°C)	Electrical energy input to heat by 1 °C in the first 5 s (J)	Heat power output in the first 5 s (W)	Efficiency in the first 5 s
Bare	(a)	0.10	4.67	0.47	32	1480	–	–	2.4	1.00	0.47	0.995
Bare	(b)	0.20	8.65	1.69	54	2020	2	975	5.2	1.64	1.69	0.997
Bare	(c)	0.30	12.94	3.90	91	2150	42	394	6.5	3.01	3.89	0.998
Bare	(d)	0.38	17.08	6.51	134	2360	106	315	8.5	3.83	6.50	0.999
Coated	(a)	0.10	2.04	0.21	26	1350	–	–	0.7	1.51	0.21	0.996
Coated	(b)	0.20	3.96	0.79	42	1850	–	–	2.6	1.53	0.79	0.996
Coated	(c)	0.31	5.98	1.83	60	1880	7	340	6.3	1.44	1.81	0.996
Coated	(d)	0.41	7.38	3.02	79	2320	14	162	9.0	1.68	3.03	0.997

The electrical resistivity was 0.11 and 0.07 Ω.cm for bare and metal-coated fiber mats, respectively. This value reflects the contact resistance at the junction of the discontinuous fibers in the mat, as well as the volume resistance of the fibers. The electrical resistance was 46.3 and 19.9 Ω for bare and metal-coated fiber mats, respectively.

Figs. 1–3 show the results for the mat with bare carbon fibers. The temperature increased smoothly with time during heating (Fig. 1). The higher the electrical power input, the higher was the temperature at the same time of heating, as expected. The temperature gradually leveled off during heating. As also shown in Table 1, the higher the electrical power input, the higher was the maximum temperature, which was 134 °C at the highest power of 6.51 W. Moreover, the higher the electrical power input, the longer was the time to reach the maximum temperature, which increased with the power input, and the longer was the time to reach half of the maximum temperature rise (Table 1). This time is referred to as the response time, the lowest of which was 2 s. The time to drop to half of the maximum temperature rise during cooling was much longer than the response time. In contrast to the response time, it decreased with increasing input power. Hence, a low input power was associated with fast heating response but slow cooling response, whereas a high input power was associated with slow heating response, but relatively fast cooling response.

The heat output is given by the electrical energy input minus the heat absorbed by the heating element (i.e. specimen). The heat absorbed is given by the product of the specific heat, mass and temperature change. Assuming that the specific heat of the specimen is constant at 830 J/kg K [14], the heat output was calculated, as shown in Table 1 for the heat released during the first 5 s of heating (i.e. the initial period of rapid temperature rise) and in Fig. 2 for the cumulative heat output as a function of the time of heating. The input electrical power essentially equaled the output heat power, as shown in Table 1 and explained below.

The ratio of the heat power output to the electrical power input is the efficiency (η) of the conversion from electrical energy to thermal energy. It is given by the equation

$$\eta = \frac{IV\Delta t - C_p m \Delta T}{IV\Delta t}$$

where ΔT is the change in temperature in time Δt, C_p is the specific heat, m is the mass, I is the current and V is the voltage. As shown in Table 1, the efficiency was essentially 1. In the initial period of rapid temperature rise (particularly the first 5 s), the efficiency increased with increasing input power. As the heating time increased, the efficiency became closer and closer to 1, as shown in Fig. 3.

Table 1 shows a comparison of the results for the mat with bare fibers and the mat with metal coated fibers. Due to the lower resistance of the coated fiber mat, the voltage and electrical power input were lower. As a consequence, the maximum temperature was lower. However, the time to reach half of the maximum temperature rise was much shorter, even when the comparison involved similar maximum temperatures. The fast response is attributed to the higher thermal conductivity due to the metal coating. The overall performance is superior for the mat with bare fibers.

The electrical energy input to raise the temperature by 1 °C during the initial portion (5 s) of rapid temperature rise was up to 3.83 and 1.68 J for bare and coated fiber mats, respectively. This value is comparable to that for flexible graphite as the heating element [15]. However, the efficiency was up to 0.999 and 0.997 in 5 s for the bare and coated fiber mats, respectively, but was up to 0.990 in 60 s for flexible graphite [15]. Hence, the time taken to approach an efficiency of 1 was less for the carbon fiber mats than for flexible graphite. On the other hand, flexible graphite provided temperatures (up to 980 °C) much higher than those provided by carbon fiber mats, probably due to the lower porosity and consequent superior heat retention ability of flexible graphite.

The overall characteristics are such that flexible graphite is superior to carbon fiber mats as a heating element. On the other hand, unlike the fiber mats, flexible graphite is not suitable for use as an interlayer between continuous fiber layers in a structural composite.

Fig. 4 shows the weight loss of the bare carbon fiber mat during heating in air. A minor loss in weight occurred at 35–85 °C. A major loss in weight occurred above 205 °C. These weight losses are attributed to the burn-off of the binder. Thus, thermal stability of the mat is acceptable up to 205 °C, which is the maximum use temperature of the mat.

In summary, a mat comprising bare short carbon fibers

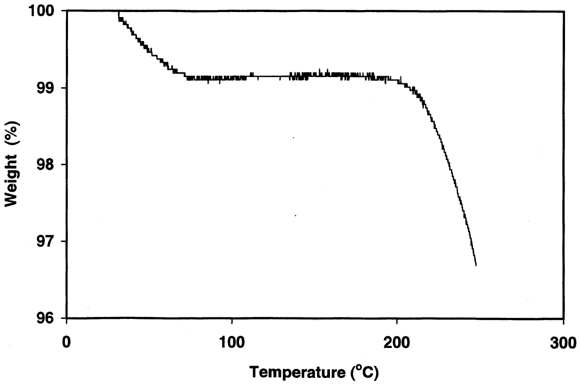

Fig. 4. Variation of the relative weight of bare carbon fiber mat with temperature during heating.

and exhibiting volume electrical resistivity of 0.11 Ω cm and thermal stability up to 205 °C was found to be an effective resistive heating element. It provided temperatures up to 134 °C at a power of up to 6.5 W, with a time up to 106 s to reach half of the maximum temperature rise. The electrical energy input to heat by 1 °C during the initial period of rapid temperature rise (5 s) was up to 3.8 J. The time to drop to half of the maximum temperature rise during cooling was much longer than the time to reach half of the maximum temperature during heating, especially when the input power was low. The efficiency of conversion from electrical energy to heat was nearly 1.00, even in the first 5 s of heating. A mat comprising Ni–Cu–Ni coated carbon fibers gave lower temperatures, due to the lower resistance, but it gave faster response.

Flexible graphite was superior to carbon fiber mats as a heating element, as it provided much higher temperatures and a much faster response.

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SWNT/PAN composite film-based supercapacitors

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Supercapacitors or electrochemical capacitors have higher power density than batteries and higher energy density than ordinary capacitors, as well as a long cycle life [1,2]. Electrically conducting metal oxide [3], conducting polymers [4], activated carbon [5], and carbon nanotubes [6–8] have been used as the active electrode materials for supercapacitors. In this letter, we report the performance of supercapacitor electrodes based on single wall carbon nanotube/polyacrylonitrile (SWNT/PAN) composite films.

A SWNT/PAN dispersion was prepared at room temperature by mixing as-produced HiPco SWNT powder [9] with a 1.5 g/l dimethylformamide (DMF) solution of poly(acrylonitrile–methyl acrylate) (90:10) copolymer (Aldrich, $M_w \sim 100{,}000$ g/mol). The weight ratio of SWNT powder to PAN copolymer is 40:60. Subsequent partial solvent evaporation from the SWNT/PAN dispersion at about 100 °C and then film casting at 85 °C in vacuum resulted in a ~10 μm thick SWNT/PAN composite film. Based on scanning electron microscopy results, the diameter of the as-produced HiPco SWNT ropes used in this

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