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Electro-Conductively Deposited Carbon Fiber for Power Controllable Heating Element

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Carbon fibers are considered as one of the promising heating elements in various industrial applications because of their excellent thermal stability and electrical conductivity. In order to achieve the controllability of the power output, gas-phase carbon deposition was carried out on the surface of carbon fiber by flowing a mixture of liquefied petroleum gas and hydrogen via electro-conduction chemical vapor deposition. We confirmed the tuning ability of the temperature ranging from 800 to 1330°C. The microtexture of the deposited carbons was sequentially changed; the initial layer with small-sized domains, the intermediate layer with medium crystallinity, and the top layer with large-sized domains and high crystallinity. However, the linear decrease in the electrical conductivity of the heating elements was ascribed to the change in the growing direction of the crystallites from longitudinal to perpendicular direction with respect to the fibers. The wide range of power output for our carbon fiber composites from 270 to 448W at 50V will be useful for various industrial electric heating applications.

Introduction

Electric heater is widely utilized in various industries and also as home appliance. Generally, the electric heating element requires two essential properties– the balanced electrical conductivity and resistance to produce optimum heat, and good thermal stability over a wide operating temperature range. Up to now, several types of electric heating elements, using metal, ceramic and carbon are commercially available.[1, 2] Among them, carbon fiber has several advantages over others, such as short response time to heat generation, high energy efficiency from highly intensive infrared radiation, high conversion rate for electricity to heat conversion (ca. 99.9 %) and high heat production (ca. 6.9 kJ).[3] Therefore, many researchers have examined various shapes of carbon fibers (e.g. filament, coil type, weaved type, and felt type) as electric heating element.[4-9]

In electric heating applications, power control has been considered as one of critical issues. Commonly, the electric power can be controlled by changing length and cross-sectional area of the heating element, and the resistivity of the applied material. When the length of the carbon heating element can be adjusted for a device, one option is to control the conduction area via a pyrolytically deposited carbon layer. Up to now, conventional chemical vapor deposition has been utilized to prepare carbon fiber/carbon composite.[10-20] Typically, four essential factors should be optimized in preparing a carbon fiber/carbon composite, which are– (a) carbon feedstock, (b) reaction temperature for deposition, (c) the type of substrate, and (d) the reaction time.[10-20] However, the conventional chemical vapor deposition requires long deposition time (up to 1 month) to achieve a high density due to its low rate of carbon deposition.[21] Thus, a

highly fast electro-conductive chemical vapor deposition is alternatively selected to obtain densely deposited carbon within a short time.

In addition, carbon fiber is selected as a resistive heating element in order to fully exploit the easy fabrication of the flexible electric heater.[22, 23] In the current paper, we will demonstrate that the cross sectional area of the heating element can be tuned by depositing pyrolytic carbon layer on the surface of carbon fibers in order to achieve the controllability of power output. Interestingly, the power output increased continuously when both the diameter and the resistivity of the heating element increased. Such an unusual phenomenon was explained by the sequential change in the direction of the crystallite growth.

Experimental section

Starting materials and synthetic methods

The carbon fibers (12K, T700 grade, Toray Co.) were used as the substrate to make carbon fiber composite as electric heating elements. Carbon fiber composite was prepared using electro-conduction chemical vapor deposition. Liquefied petroleum gas was used as the carbon source, hydrogen was included to accelerate the deposition rate and argon was used as a carrier gas. Total gas flow was fixed at 2000 mL/min, and the mixture ratio of liquefied petroleum gas/hydrogen/argon was 1/2/2. Electro-conductive chemical vapor deposition apparatus was designed by modifying conventional chemical vapor deposition chamber (Plus Co Lab, Korea). The carbon fiber composites

were fabricated by varying the voltage from 50 to 120V and also the reaction time from 5 to 30s. A detailed experimental procedure and conditions have been described in Fig. S1.

Characterizations

The cross-sectional morphology of the pristine and carbon fiber composites prepared at various conditions was characterized using a Hitachi S-4700 field-emission scanning electron microscope (FE-SEM). The microtextural changes before and after electro-conductive chemical vapor deposition were evaluated using a TEM (TECNAI F20, FEI, USA) with an acceleration voltage of 200 kV. TEM samples were prepared using focused ion beam milling techniques (Helios 460L, FEI). The structural integrity of the carbon fiber composites was characterized by an X-ray diffractometer (XRD, D-Max-2400 diffractometer) equipped with graphite monochromatized CuK_α radiation (λ = 0.15418 nm). Backscattering Raman measurements were carried out with an *inVia* Reflex UV Raman microscope (Renishaw, UK, 633 nm) which is situated at KBSI (Gwangju-center, Korea). Electrical resistance was evaluated by modified conduction chemical vapor deposition equipment (Plus Co Lab, Korea) in DC voltage.

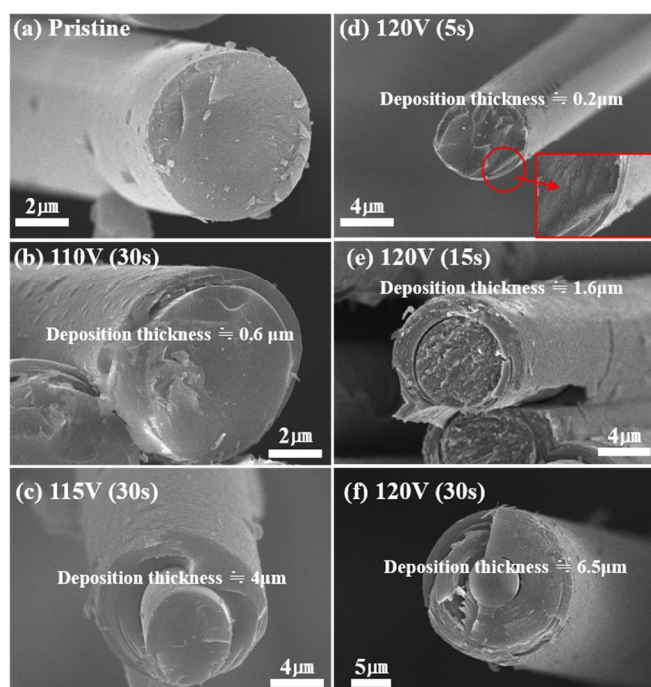## Results and discussion

Fig. 1 FE-SEM images of (a) pristine carbon fiber, carbon fiber composites prepared, (b) at 110V for 30s, (c) at 115V for 30s, (d) at 120v for 5s, (e) at 120V for 15s and (f) at 120V for 30s, respectively

The heating elements were prepared by exposing carbon fibers to a mixture of liquefied petroleum gas and hydrogen under electro-conductive heating under various conditions, where the deposition time was varied from 5 to 30s at 120V, and the voltage from 110, 115 to 120V for 30s. The morphological change in the carbon fibers before and after electro-conduction chemical vapour deposition was examined

using FE-SEM (Fig. 1). The pristine fiber (Fig. 1 (a)) shows smooth surface, whereas deposited carbons on the surface of carbon fibers show clearly different morphology (Figs. 1 (b-f)). The thickness of the deposited layer increased continuously from 0.2 to 6.5μm with increasing voltage and deposition time. To estimate the energy required for the deposition, activation energy was obtained from the Arrhenius plot (453 kJ/mol, see Fig. S3)

In conventional chemical vapor deposition, the substrate is heated to high temperature using heating element and exposed to volatile precursors, which decompose on the substrate surface. Thus, several processing parameters, such as temperature, deposition time, pressure and surface area should be controlled.[24] In contrast, the electro-conductive chemical vapor deposition used the substrate itself as heater (*e.g.*, carbon fiber) and thus the volatile gases are deposited on the heated substrate homogeneously within a short time. Therefore, only two parameters, such as voltage and deposition time, should be optimized. Variations in temperature and current were measured as functions of the voltage and deposition time (Fig. S2). When the voltage was changed from 110 to 120V, the temperature of the carbon fiber composites is changed from 800 to 1150°C. The linearly increased amount of deposited carbon with increasing voltage indicated an enhanced cracking rate of hydrocarbon at higher temperature.[25, 26] As the deposition time (at 120V) increased (Fig. 1 (d-f)), deposition thickness also increased linearly from 0.2 to 6.5μm. We observed a linear change in the temperature with the reaction time (Fig. S2 (a)).[27] It is believed that the enlarged diameter of carbon fiber caused by the deposited carbon in the gas phase would largely increase the temperature of the heating element. Interestingly, the variation of temperature was quite different from the thickness of deposited carbon. Temperature gradually increased until 15s of reaction time, and then slightly decreased between 15 and 30s reaction time, even though deposition thickness increases steadily from 0.2 to 6.5μm. This moderately decreased temperature is probably due to the microstructural changes from fine to coarse structure accompanying with the improved crystallinity that occurred between 15 and 30s of the reaction time.

To understand the electrical properties of the carbon fiber composites, we measured resistance at 50V and then calculated both the electric power at 50V and the resistivity. When calculating resistivity (ρ = Ω A/L (Ω: resistance, A: dimension, L: length)), the thickness of the deposited carbon layer was obtained from FE-SEM observation. The resistance at 50V, deposition thickness, resistivity and electric power at 50V are summarized in Table 1.

Table 1 Resistance and resistivity values (at 50V) of carbon fiber composites prepared under various conditions.

	Applied voltage (V)				Deposition time (sec)			
	Pristine	110V (30s)	115V (30s)	120V (30s)	Pristine	120V (5s)	120V (15s)	120V (30s)
Resistance (Ω) at 50V	9.26	7.96	5.75	5.58	9.26	7.99	6.47	5.58
Deposition thickness (μm)	0	0.60	4.00	6.50	0	0.20	1.60	6.50
Resistivity (x 10^{-4} Ω·cm)	1.43	1.68	4.06	7.01	1.43	1.37	2.11	7.01
Electric power (W) at 50V	270	314	435	448	270	313	386	448

The resistance decreased from 9.26 to 5.58 Ω as both the voltage and the deposition time increased. This can be ascribed to the enhanced deposition rate of carbon on the surface of carbon fibers with increasing time and voltage, thereby causing an increased cross-

sectional area of the fibers and the crystallinity of the deposited carbon also predominantly contributed to the reduction in resistance.[27] We also observed that the electric power continuously increased from 270 to 448 W at 50V with increasing voltage and reaction time. This phenomenon can be explained easily from the equation of electric power (W), $W = V^2/R$ (V=voltage, R= resistance). The steady decrease in resistance can be explained by the enlarged cross-sectional area of the carbon fiber due to the electro-conductively deposited carbon, thus it can be said that electric power is significantly affected by the thickness of the pyrolytically deposited carbon.
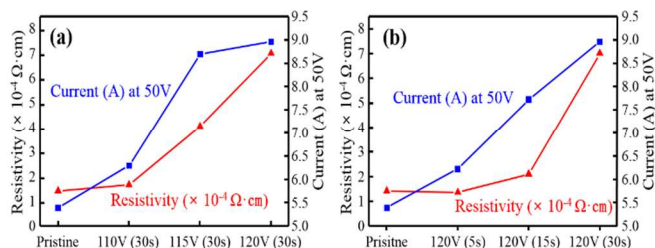

Fig. 2 Variations of resistivity and current (a) as a function of applied voltage (where reaction time is fixed for 30s), and (b) as a function of deposition time (where applied voltage is fixed at 120 V).

Figure 2 shows the variations of resistivity and current as a function of the applied voltage and deposition time. Generally, resistivity and current show an opposite behavior at constant voltage. However, we observed a linear relationship between resistivity and current, as shown in Fig. 2 (a, b). This implied that the pyrolytically deposited carbon showed different microstructure, thereby resulting in the change of electrical properties.
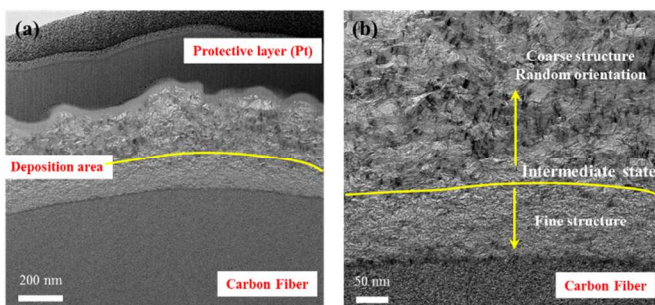

Fig. 3 Cross-sectional TEM images of carbon fiber composites (prepared at 120 V for 30 s) (a) at a low-magnification, and (b) at a high magnification.

To evaluate the microstructure of the deposited carbon, TEM analysis was carried out. As shown in Fig. 3, the deposited carbon displayed a boundary line with a thickness of 200 nm on the surface of carbon fiber. In addition, we observed that the deposited carbon consists of two phases, fine and coarse structures. Initially, the deposited carbon showed (see yellow down arrow in Fig. 3 (b)) small-sized domains (called as fine structure), then through an intermediate state, large-sized but randomly distributed domains with large curvature (called as coarse structure) were formed, as observed clearly in the deposited carbon (see yellow up arrow in Fig. 3 (b)). Such large-curved domains observed in coarse structure possibly come from the abruptly increased reaction temperature

because the change of growth direction of the crystallites from parallel to perpendicular to the fiber direction leads to a large increase in the electrical resistivity of carbon fiber heating material.[28-30]
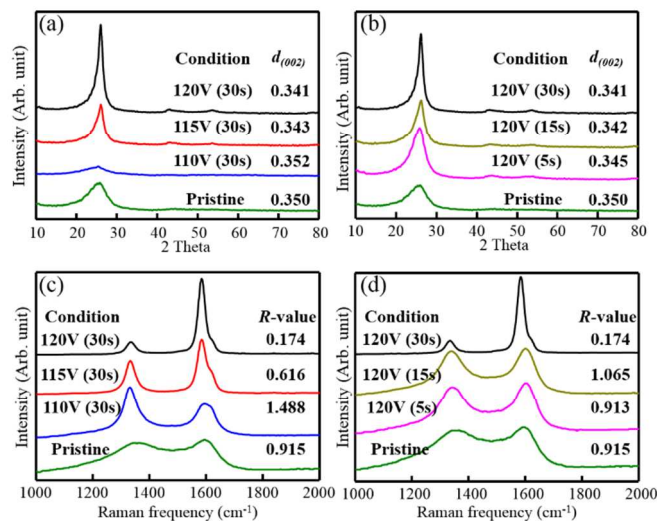

Fig. 4 (a, b) X-ray diffraction patterns, (c, d) Raman spectra of the pristine carbon fiber and carbon fiber composites prepared at (a, c) different voltages, and (b, d) different reaction times.

To analyse the above-mentioned microstructural change in the deposited carbons in more detail, X-ray diffraction patterns (Fig. 4 (a, b)) and Raman spectra (Fig. 4 (c, d)) were recorded. A strong (002) diffraction line in the range 20° - 30° was observed for all the samples. The decreased interlayer spacing ($d(002)$) with increasing applied voltage and deposition time signified a continuous increase in the crystallinity of the deposited carbon with increasing applied voltage and the deposition time. From Raman spectra (Fig. 4 (c, d)), there were two strong peaks at 1330 cm^{-1} (D-band, defect induced mode) and at 1580 cm^{-1} (E_{g2g} mode). As both the applied voltage and deposition time increased, both intensity and full width at half maximum (FWHM) of the D-band decreased continuously, whereas the intensity and the FWHM of the G-band increased and decreased, respectively. Moreover, R value (I_D/I_G, the integrated intensity of the D-band divided by the integrated intensity of the G band) decreased from 0.915 to 0.174, indicating the continuously improved crystallinity. Note that the Raman spectra are well consistent with the XRD result. Structural parameters (*e.g., R* value and interlayer spacing) shows a decreased tendency when carbon fibers are exposed to longer deposition time and higher voltage during electro-conduction chemical vapor deposition. However, carbon fiber heating elements that are prepared at 110V for 30s and at 120V for 15s exhibited low crystallinity. The large R value and interlayer spacing of the sample prepared at 110V for 30s can be ascribed to temperature effect in electro-conductive chemical vapor deposition. Generally, hydrocarbons under high-temperature conditions are first dehydrogenated and then deposited on the surface of the substrate. Eventually, the deposited carbons condense and polymerize to form large solid carbons.[17, 31] The temperature and current of carbon fiber heater were *in-situ* measured during the electro-conductive CVD reaction (Fig. S2). At 110V, the temperature is enough for carbon deposition but is too low to achieve a graphitic structure. Thus undeveloped carbon was deposited on the surface of carbon fiber at 110V for 30s. At 120V, the effect of reaction time on the properties of carbon fiber heating element is quite different from general trend of our samples. We found that temperature showed an increasing

tendency with increasing reaction time. Specifically, the temperature showed a gradual increase for the first 5s reaction, and then it started increasing rapidly when the reaction time was between 5 and 15s. Considering the effect of temperature on chemical vapor deposition mechanism, we assume that, during the reaction time between 5 and 15s, an enhanced deposition rate of carbon contributed to sharp increase in the temperature. It is believed that carbon fiber prepared at 120V for 15s is closely related with the intermediate state. Therefore, the highest R value is obtained for the sample prepared at 120V for 15s, indicating the formation of undeveloped structure due to an abrupt chemical reaction.[31] Microstructure of deposited carbon strongly depends on the reaction temperature.[28-30] In case of gas-phase pyrolytic carbon formation, the deposited carbon had small-sized domains at low temperature, but large-sized domains at high temperature. We observed small-sized and undeveloped fine structure until the specified thickness of deposited carbon or time was reached (at 120V for 15s). Therefore, enlarged surface area (or fiber diameter) of carbon fiber contributed directly on the temperature rise in electrically-conducted carbon fiber heating element. Resultantly, high reaction temperature exerted a huge effect on the structural density and microstructure of deposited carbons.

To evaluate the temperature variation of carbon fiber heater at 120 V, both power output and temperature of electro-conductively deposited carbon fiber heater at 50 V are plotted as a function of applied voltage and deposition time (Fig. S4). The continuous increase in the deposited thickness of deposited carbon leads to the reduction of resistivity. By borrowing the power equation ($P = V^2/R$), we confirmed the continuously increased power as a function of deposited time at a fixed voltage. Eventually, we obtained the linear relationship between power output and temperature (Fig. S4).
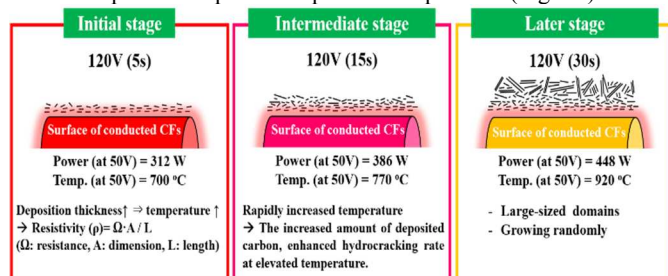

Fig. 5 Suggested growth mechanism of the deposited carbon on the surface of carbon fibers during electro-conduction chemical vapour deposition.

Finally, we proposed the growth mechanism of the deposited carbon during electro-conduction chemical vapor deposition (Fig. 5). We believe that the deposited carbon grows via three stages in electro-conductive chemical vapor deposition. Initially, undeveloped small-sized domains were mainly deposited as fine structure on the surface of carbon fiber. Such deposited carbon leads to the change in reaction temperature, based on the resistivity (ρ) equation (due to the increased dimension). In the intermediate stage, the temperature increases sharply when the carbon fiber is electro-conductively treated at 120V for 15s. Thus, the amount of deposited carbon increases rapidly due to an enhanced hydrocracking rate of hydrocarbon. In addition, some undeveloped carbon is formed at this sudden rise in the reaction temperature. Finally, the hydrocarbon is deposited to form randomly grown carbon with large-sized domains.

Conclusions

Herein, carbon fiber composites were fabricated by passing electricity along carbon fiber bundle to examine its potential as heating element with the controllability of the output power (Fig. S5). We observed three important things in ours study– (1) the activation energy of electro-conductive chemical vapour deposition was 376 kJ/mol, (2) the controlled thickness of the deposited carbon (0.2 to 6.5μm) allowed carbon fibre composites to have the wide range of electric power from 270 to 480W at 50V and (3) the microstructure of the deposited carbon on the surface carbon fibre strongly depended on both voltage and reaction time. As a result, we believe that carbon fiber composites prepared by electro-conductive chemical vapor deposition can be used in commercial heating element, because of their short fabrication time and high ability of controlling the output power.

Acknowledgements

Notes and references

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