JOULE HEAT TREATMENT ON CARBON NANOTUBE FILMS AT DIFFERENT ELEVATED TEMPERATURES

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ABSTRACT

The temperature response and material changes of Joule heat on carbon nanotube (CNT) films are studied at different elevated temperatures. The results indicate that Joule heating causes rapid rise of temperature up to 300ºC/s for the CNT film. Meanwhile, the steady temperature shows an approximate linear relationship with the power. Under long-term Joule heating the resin impregnated CNT film turns into a well cured CNT composite film. However, uneven temperature distribution of the film is recognized during the Joule heating process, and the temperature distribution can't be changed by simple pressing, stretching and impregnation on the CNT film. It reveals that the square resistance is the main factor affecting the temperature distribution of the film. In addition, the Joule heat treatment below 250ºC results in an increase of the thickness by 10% and a decrease of the electrical conductivity by 15% for the CNT film.

1 INTRODUCTION

Since carbon nanotubes have been found [1], carbon nanotubes and its composite materials have been very widely used in the fields of information, electronics, aviation, aerospace and other fields, because of excellent mechanical [2], electrical [3], thermal [4], damping [5] and other properties. As a two-dimensional macroscopic structure, CNT film can avoid random aggregation and difficult dispersion of the nanotubes, providing a non-damaged native structure and high-load of nanotubes. Thereinto, floating catalytic chemical vapor deposition is a highly efficient, continuous producing and easily scale-up method for fabricating high performance CNT films.

Carbon nanotube films composites were usually prepared by the oven or hot pressing method [6-9]. High power consumption existed in these processes, which was not conducive to the green preparation and development of materials. The development of the resistive heating process with Joule heat could significantly reduce the energy consumption by 95%. Jae-Woo Kim [10] successfully fabricated CNT/thermosetting nanocomposite films by resistive heating assisted penetration and curing (RHAIC) of polymer matrix resin. The highest specific tensile strength and Young's modulus of this RHAIC

CNT/Bismaleimide (BMI) composite films were 684 MPa/(gcm^{-3}) and 71 GPa/(gcm^{-3}), respectively. Jeonyoon Lee [11] utilized aligned CNT film-integrated heaters to cure polymer composites. While achieving the same degree of cure, this method significantly reduced energy consumption compared to in-oven curing. Nam Nguyen [12] successfully prepared carbon fiber / buckypaper hybrid composites by in situ Joule heating with buckypaper. The results indicated that hybrid composites fabricated by this in situ curing method exhibited relatively good mechanical properties and low void content。

Although the resistive heating process of carbon nanotube films has been researched and applied in some fields, the temperature response and the factors that affect the uniformity of the heating temperature are rarely studied. The changes of the carbon nanotube films before and after heating at low temperature (room temperature to 300ºC) are also unintelligible. In order to further evaluate the reliability of resistive heating of Joule heat as a composite process method, the Joule heating rate and the steady temperature of the carbon nanotube films at different power levels were discussed. The long-time temperature stability was also studied. During this research, it was found that the temperature distribution of the carbon nanotube film was not uniform during the resistive heating. Therefore, the factors influencing the temperature distribution of the carbon nanotube films during resistive heating were further explored. On the basis of this, the structure and composition of the carbon nanotube films were investigated by heating the films which had uniform temperature distribution at different elevated temperatures. These findings could be beneficial for further study and be utilized on the low energy consumption preparation of nanocomposites and fiber-reinforced composites.

2 MATERIALS AND EXPERIMENTAL SECTION

2.1 Materials

The carbon nanotube films were prepared by floating catalytic chemical vapor deposition. The carbon nanotubes, provided by Suzhou JieDi nanometer technology company, had 5-7 walls, and the thickness of the films was about 10μm. Carbon nanotube / Bismaleimide prepreg films were obtained by immersing the carbon nanotube films in 1 wt% or 5 wt% BMI / DMF solution at 30°C for 1 h. After immersing, the films were dried for 12 h and then heated by current. About press treatment, the carbon nanotube films were pressed using a flat vulcanizer, and the pressure applied on the surface of the carbon nanotube films was 200 MPa.

2.2 Joule heating

Copper foils were pasted on the both sides of the 45mm × 6mm wide carbon nanotube film using conductive silver paste. The wires were used to connect both ends of the copper foils to the positive and negative terminals of the Agilent U8002A 30V 5A DC power supply. The temperature and infrared image of the heating process were collected by a IRS infrared imager. Heating and temperature acquisition devices were put in a closed enclosure. Temperature was set to constant to reduce convective heat transfer from film to the air during heating.

2.3 Characterization

The electrical conductivity and square resistance of carbon nanotube films were tested using RTS-9 four-probe tester. The JEOL JSM7500F field emission scanning electron microscope (FESEM) was utilized to obtain the secondary electron image of the carbon nanotube films. The acceleration voltage was 3kV and the working distance was 7-9mm. The thickness was tested using a spiral micrometer and verified using scanning electron microscope. The thermogravimetric analysis was implemented with a NETZSCH STA 449 synchronous thermal analyzer with a heating rate of 10 °C /

min.

3 RESULTS AND DISCUSSION

3.1 Electro-thermal Response of Carbon Nanotube Films

A 3W constant power was applied to a 45mm × 6mm carbon nanotube film, and infrared images were collected at the fastest acquisition frequency of 0.2s / frame using an infrared imager. The three consecutive images were collected and shown in Fig.1 (a) - (c). The results of Fig.1 (d) were obtained by taking the average temperature of the three evenly spaced points on the film to make time-temperature curve. The curve slope of 304.33 was the heating rate of the resistive heating of carbon nanotube film, which is higher than 300ºC/s. Such a high heating rate was mainly due to the small film quality. The surface density of the carbon nanotube film was only 5g /m^2 and the experimental film was only about 1.4mg. The heat that the film required was much smaller than that of Joule heat, which caused the temperature of the film increasing rapidly and fast balanced after power supply. When the temperature maintained within 5ºC, we assumed that the temperature reached the steady temperature at that power.

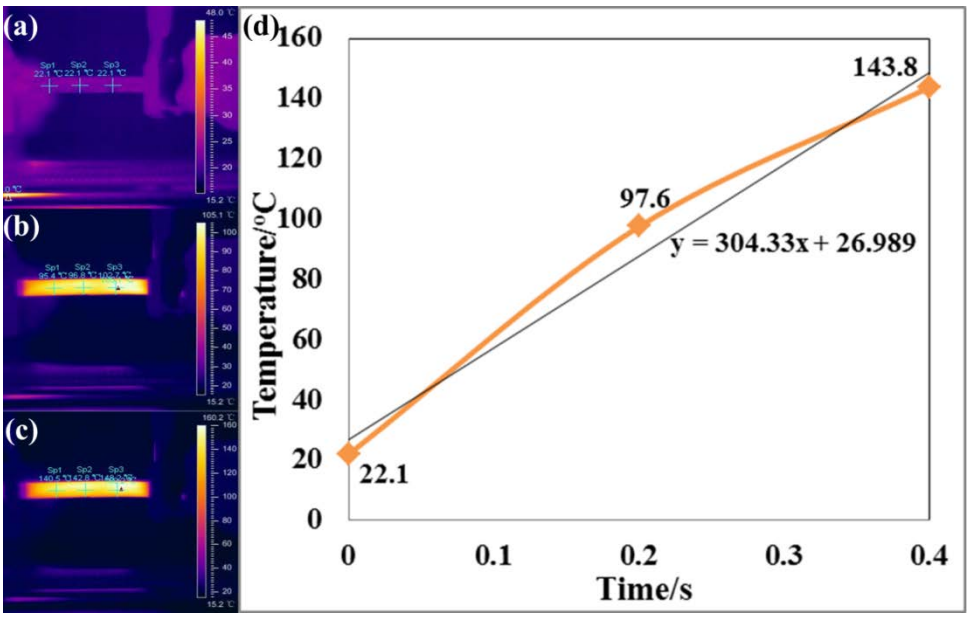

Fig. 1 (a) (b) (c) Infrared thermal image of three consecutive frames at 0.2 s / frame at 3 W power; (d) Heating rate curve of resistive heating of carbon nanotube film.

The carbon nanotube film could reach steady state within 1 second, and the heating time was much smaller than the holding time. Compared to the entire heating stage, the temperature rise stage was negligible. To this end, we focused on the power-steady temperature relationship of the carbon nanotube film. As shown in Fig.2 (a) (b), we studied the power-steady temperature relationship about pure carbon nanotube films and films impregnated with 1 wt% BMI/DMF solution. The results revealed that two kinds of materials had approximate linear relationship with the steady temperature in the range of room temperature to 300ºC. When the temperature was lower than 150ºC, the linear relationship was especially prominent. The linear relationship was weakened while the temperature increased. We also found that the difference between the maximum temperature and the minimum temperature on the film increased with the rising power supply. Difference on the pure film was more serious than that of the BMI resin impregnated film. In the curing process of composite films, excessive temperature difference is unfavourable for uniform resin curing and will lead to the

generation of internal stress. To ensure the cure uniformity, we studied the factors that affected the film temperature distribution, which will be described later in details.

In order to investigate the temperature stability of the resistive heating process with constant power and ensure the resin could be cured by using this method, the carbon nanotube films impregnated with 1 wt% BMI/DMF and 5 wt% BMI/DMF solution were subjected to a 2h heat of 220 °C temperature with the resistive heating process. The results were shown in Fig.2 (c) (d). The temperature of different positions on the film kept approximate constant during the heating process, but there was still a certain temperature divergence between different points. The 5wt% BMI impregnated film fluctuated greatly at the first 1h, which may owing to the higher resin content. Although certain temperature fluctuations emerged, the heating process maintained a constant range of temperature. The temperature fluctuation was less than 10 °C, so this method could be took use of on the preparation of nanocomposites.

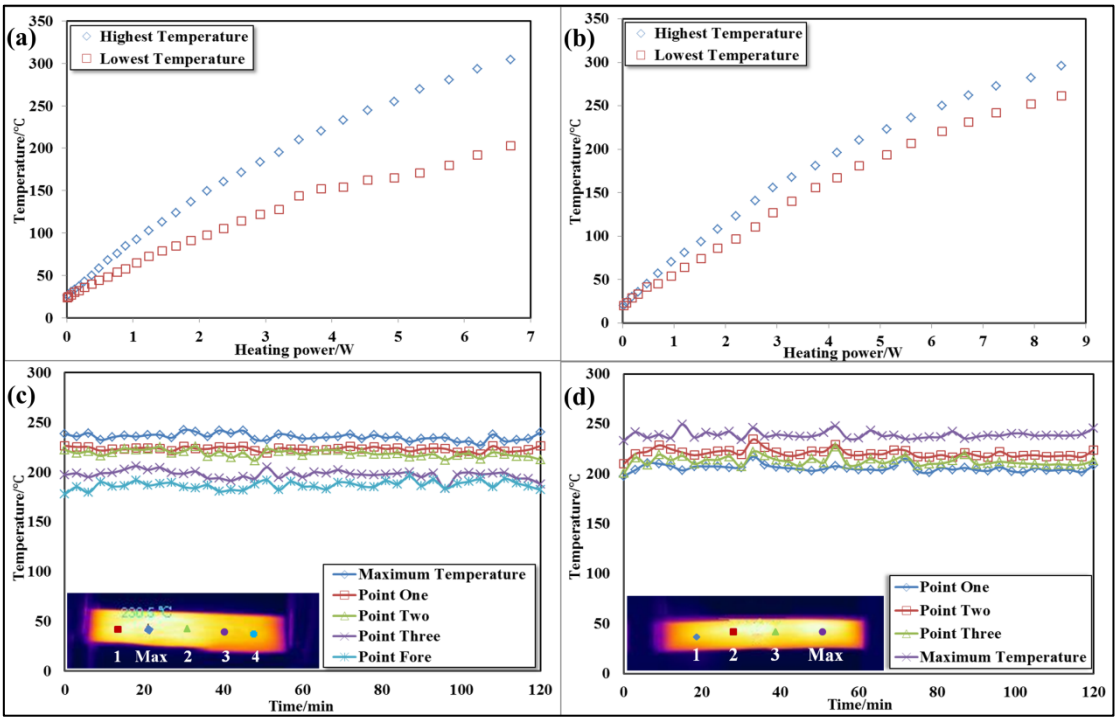

Fig.2 (a) Power-steady temperature curve of pure carbon nanotube film,(b) Power -steady temperature curve of 1 wt% BMI / DMF solution impregnated carbon nanotube film,(c) Resistive heating time-temperature curve of 1 wt% BMI / DMF solution impregnated carbon nanotube film,(d) Resistive heating time-temperature curve of 5 wt% BMI / DMF solution impregnated carbon nanotube film.

3.2 Factors of Temperature Distribution of Carbon Nanotube Films

The previous studies showed that there was a large temperature difference between the various locations of the film during the resistive heating of Joule heat. The inhomogeneous temperature distribution was unfavorable for resin curing and would affect the quality of the composites. To change the uniformity of the temperature when heating, we studied the effect of high pressure press, stretch, and resin impregnation on the temperature distribution by using a same carbon nanotube film. The results were displayed in Fig.3. The treatment changed the overall resistance of the film, which caused the current changed with the same voltage and the steady temperature changed, but the temperature distribution on the film remained essentially unchanged. The temperature of the left side is low and the right side is high in the Fig.3.The high temperature region cannot be easily changed through the

various treatments of 200 MPa high pressure pressing, 10% stretching, and 5 wt% BMI solution impregnating.

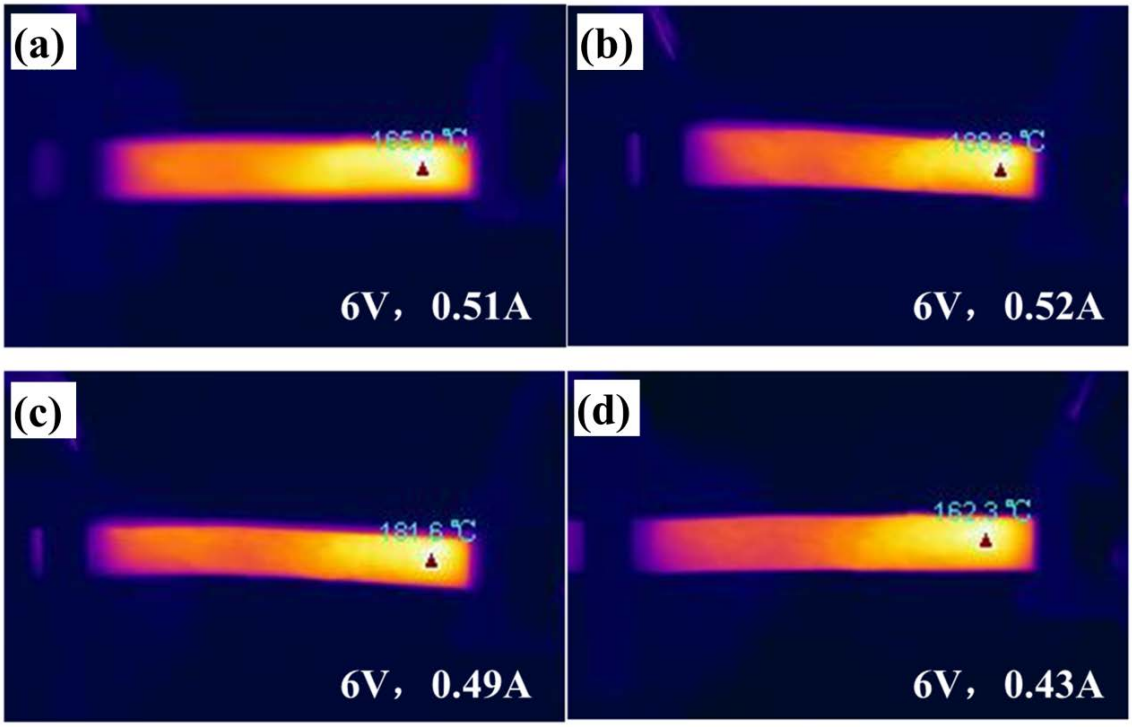

Fig.3 Infrared thermal image at 6V Voltage of carbon nanotube film (a)native,(b)native+200MPa pressing,(c) native+200 MPa pressing+10% stretching,(d) native +200MPa pressing+10% stretching+5 wt% BMI solution impregnated.

Based on the above results, it is necessary to find the factors that affect the temperature distribution of the film, which can guarantee the curing uniformity of the resin. The pure carbon nanotube film and 5 wt% BMI impregnated carbon nanotube film were employed for this study. The relationship between the heating temperature of the different positions and the resistance of these position was shown in Fig.4. When eliminated the anomalies caused by the edge effects of the film，the outcome indicated temperature distribution and square resistance distribution change synchronously. The square resistance value on the different positions of the film was the main factor affecting the temperature distribution. While Joule heating power exist a relationship: $P = I^2R$, the film could be regarded as a series circuit. Because of the same current, the different position resistance directly affected the heating power and the relationship was linear. The previous studies indicated that the temperature at the heat balance was approximately linear with the heating power, so the square resistance and the heating temperature at that position also realized a linear relationship. The distribution of the square resistance directly affected the temperature distribution of the film in resistive heating. The treatments such as pressing, stretching and impregnating of the film could only change the absolute value of the square resistance, but it was difficult to change the distribution of the square resistance among different positions. Hence, the uniformity of the temperature distribution cannot be tailored and improved by simple pressing, stretching, and impregnating.

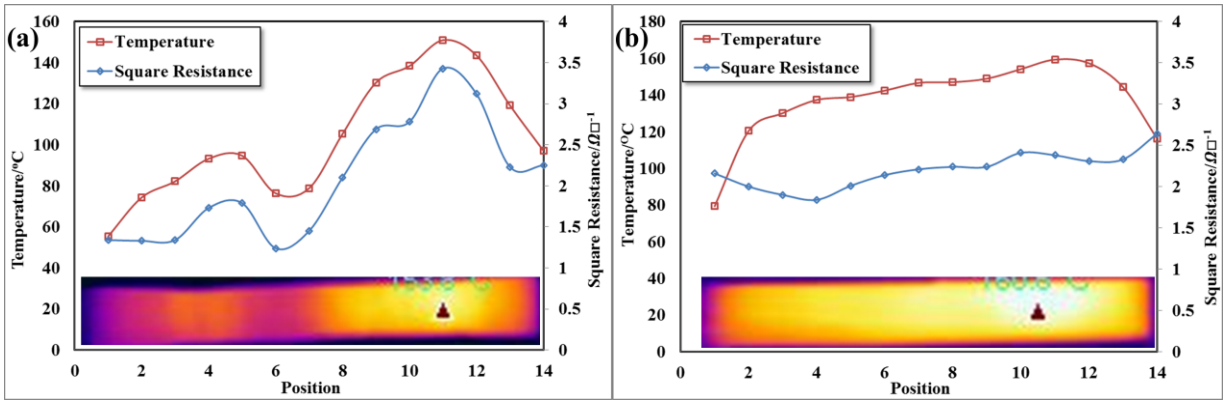

Fig.4 (a) The corresponding relationship of square resistance-steady temperature in different positions of pure carbon nanotube film; (b) The corresponding relationship of square resistance-steady temperature in different positions of 5wt%BMI impregnated carbon nanotube film.

The FCCVD carbon nanotube film is prepared by spun the aerogels on a mandrel with simultaneous solvent spraying densification. Several hundred turns are applied during the process, but winding tension, thickness and uniformity of spray solvent are inevitably different, which makes the non-uniformity of the square resistance. Therefore, we need testing the distribution of the square resistance to evaluate the uniformity of the temperature distribution of the film. Selecting the uniform resistance of the film can lead to the uniform temperature distribution during heating and be benefit to the quality of composite materials.

3.3 Structure and composition of carbon nanotubes before and after heat treatment

The film with uniform temperature distribution was selected by measuring the distribution of the square resistance. Then the thickness and electrical conductivity of the films treated by Joule heat at 100°C, 150°C and 250°C were characterized respectively. The results were showed as Fig.5 (a). It suggested that the thickness of the films increased 17.5%, 10.0% and 10.1% respectively when treated at 50°C, 150°C and 250°C for 1h, but the electrical conductivity decreased 12.1%, 16.4% and 15.8% respectively. The increase rate of the thickness gradually decreased but the decrease rate of the electrical conductivity increased with the increasing of the heating temperature.

The scanning electron microscopy (SEM) of the films that were native and treated with Joule heat at 50 ° C, 150 ° C and 250 ° C were observed as shown in Fig. 5 (b)-(e). The size of the catalyst particles in the films of native and treated at 50°C was large, but it decreased with the increasing of the treatment temperature. It could also be seen that the pore size of the film was reduced to some extent when heating temperature increased.

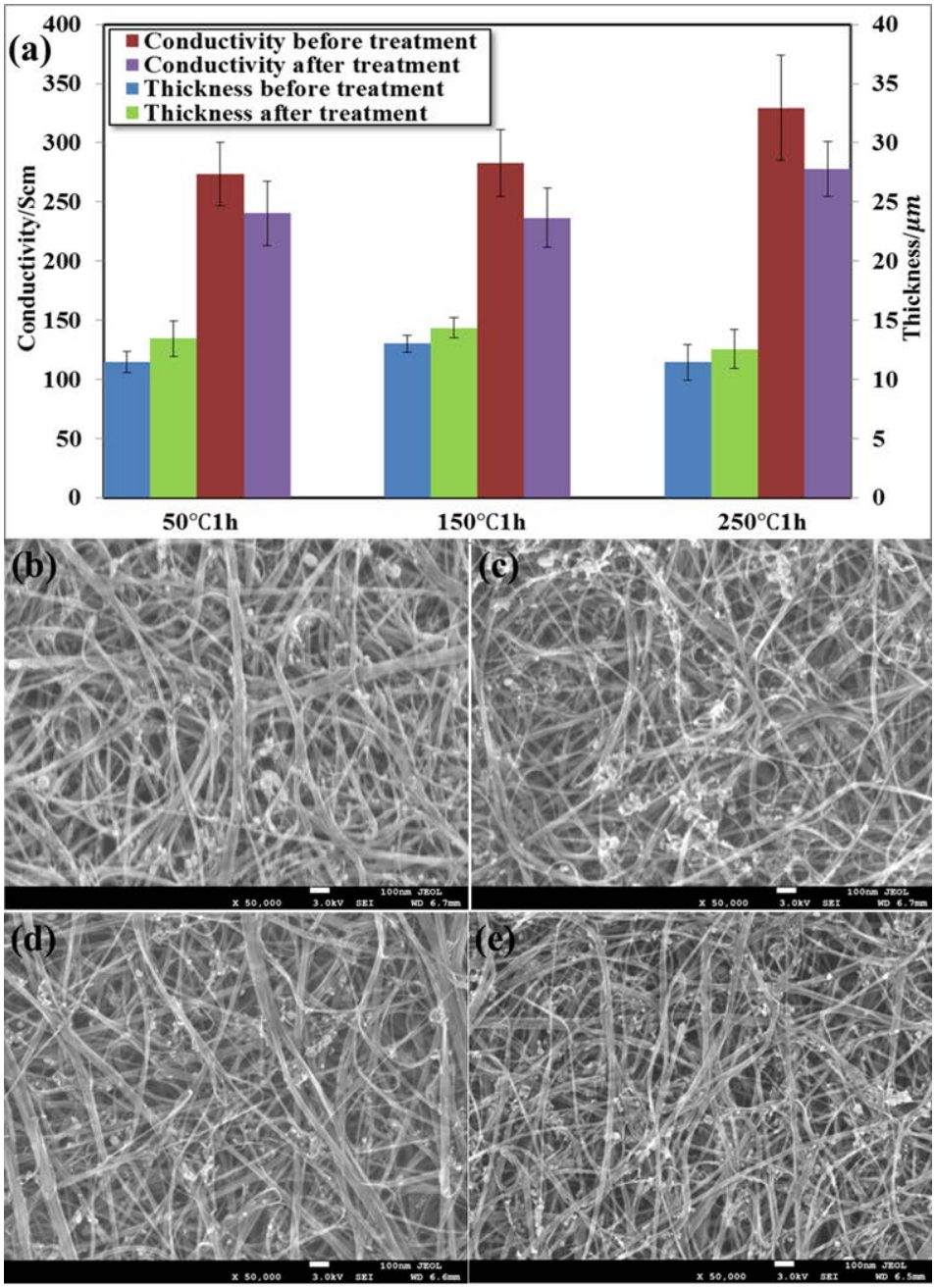

Fig.5 (a) Electrical conductivity and thickness change of carbon nanotube films after different temperatures treatment; SEM image of carbon nanotube film (b) native (c) 50°C (d) 150°C and (e) 250°C 1h Joule heat treatment

CONCLUSION

Resistive heating with Joule heat on carbon nanotube film is an excellent process method with fast heating, fast balance and good temperature-power linear characteristics. This process method has good long-term heating stability and can be utilized on curing the resin impregnated CNT film composite. The square resistance distribution is the main factor that affects the temperature distribution of the film during the heating process. It is difficult to change the uniformity of the temperature distribution by treating the film such as pressing, stretching and resin impregnating. The experiments showed that the Joule heat can change the thickness and the electrical conductivity of the

carbon nanotube film during the process.

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