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Preparation of Large Scale Electrical Conductive Composite Film with Alinged Carbon Nanotubes Using AC Electric Field

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***Abstract*—Electrical properties of dielectric materials, such as permittivity or conductivity, can be adjusted by adding appropriate filler into the dielectric matrix. In this study, multi-walled carbon nanotubes (MWCNTs) were aligned in ultraviolet (UV) cured epoxy resin by exerting AC high electric field to fabricate a composite film. In order to clarify the relationship between MWCNTs alignment under AC high electric field and the electrical properties of the epoxy resin, the dependence of the network formation and the resistivity of film upon applied electric field time and the frequency were investigated. Based on a simulation of electric field distribution, a new type of array of parallel electrodes was designed to preparing large scale, in plane aligned MWCNTs conductive composite film. The experiment results showed that MWCNTs aligned and formed conductive network between each pair of the electrodes along the direction of electric field. The resistivity of cured MWCNT/epoxy composite film decreased three orders of magnitude than that of without electric filed application.**

Keywords-alignment; carbon nanotube; composite film; electric field; resistivity

I. INTRODUCTION

Carbon nanotubes (CNTs) as one kind of nanoscale filler have attracted significant attention. In summary, the following three properties of CNTs are specifically interesting for the industry. Firstly, CNTs can be used to improve mechanical properties of polymers without increasing their weight due to their outstanding mechanical strength and low weight density [1]. Secondly, high thermal conductivity of CNTs can be used to improve the thermal conductive properties of polymers [2, 3]. Thirdly, the excellent electrical properties make CNTs suitable for forming conductive network in polymer matrix [4]. A combination of these superiorities promotes CNTs as a replacement of conventional materials such as carbon black and carbon fiber. The application of conductive composite materials composed of CNTs and polymer matrix are already a commercial reality [5]. The CNTs have intrinsic anisotropy because of their high aspect ratios. Therefore, it is possible to take advantage of these facts to manipulate CNTs. Composites with aligned CNTs can lead to such a variation in anisotropic electrical properties [6, 7] and thermal conductivity properties [8]. For example, dispersion of CNTs in a polymer and deposition them onto device substrates, are necessary to realize their application for large scale distributed electronics such as steerable antenna arrays [9], flexible displays, electrostatic charge dissipation [10] and electromagnetic shielding applications [11]. In order to realize CNTs/polymer composites with high electrical performances, good dispersion, well alignment and electrical conducting path of CNTs in polymer matrix should be achieved. Some approaches have been investigated on the alignment such as carbon blown bubble film process [12], mechanical stretching [13], blending mixing [14], layer-by-layer assembly and combining [15, 16], liquid crystal assisted orientation [17], electric field [18, 19] and magnetic field [16, 20], respectively. Many researches have been carried out on the effect of CNTs loading fraction, percolation threshold, dispersion state, functionalization of CNTs and polymer curing process.

Electric field induced alignment of CNTs network is an efficient and direct route to prepare CNT/polymer composite materials. A pair of parallel electrodes with spacing from millimeter to several centimeters is widely used to apply electric field on matrix [18, 19, 21-22]. However, large scale film is difficult to prepare by using the one pair of parallel electrodes because of the necessarity of high voltage source for wider electrode gap. It limits the application and practicability. In this study, UV-cured epoxy resin was employed to prepare the conductive composite film. Firstly, we investigated the optimum conditions of application time of electric field and the influence of frequency on conductive network formation when using a pair of parallel electrodes. From the view of practical application, a new type of array of parallel electrodes was designed to prepar large scale aligned CNTs conductive composites film.

II. EXPERIMENT

A. Materials

The MWCNTs used in this study were synthesized by chemical vapor deposition (Aldrich, US), which had a diameter of 7-15 nm and a length of 0.5-200μm. The effective particle size of MWCNTs was 57 μm, which was measured by a particle size analyzer (Shimadzu Sald-7100, Japan). The composition carbon content is above 95%. The MWCNTs were used without futher purification or modification. The UV-cured epoxy resin with a viscosity of 400cps was purchased form Tesk Co.Ltd (Japan). The resistivity of pure cured epoxy is about 10^{10} Ωm. 0.05 wt.% MWCNTs was dispersed in uncured epoxy resin by ultrasonication for 6h.

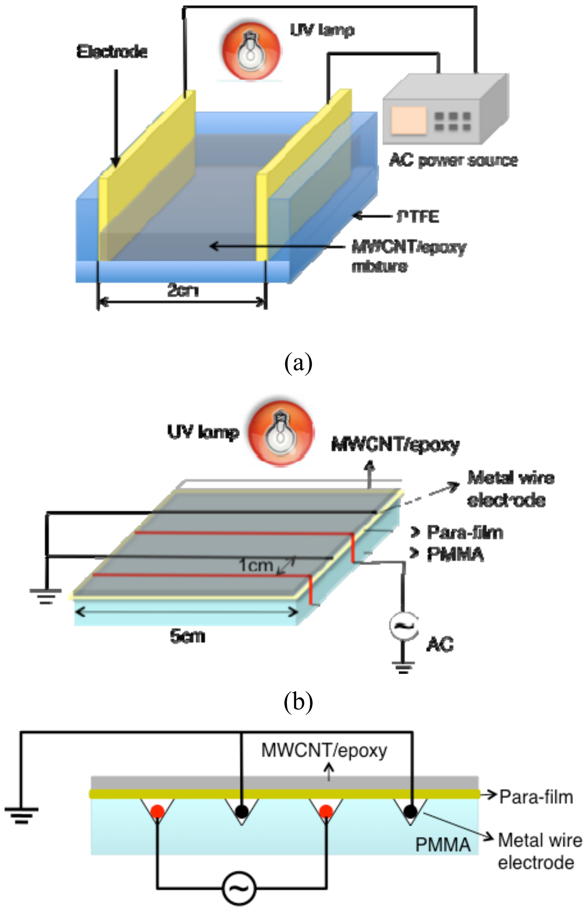

Figure 1. The experiment setup (a) A pair of parallel electrodes. (b) Schematic and (c) Cross section of array of parallel of electrodes.

B. Preparation of MWCNT/epoxy composites film

1) A pair of parallel electrodes

Figure 1 (a) shows the experiment setup using the parallel electrode system. About 1 mm height of mixture was poured into a polytetrafluoroethylene (PTFE) chamber. AC voltage of 4 kV was applied between two parallel steel electrodes which gap distance was 2 cm. After applied electric field for desired time, a UV lamp (365nm wavelength, Vilber Lourmat, VL-215.LC, US) was started to make epoxy cured and preserve CNTs network in epoxy film.

2) Array of parallel electrodes

Figures 1 (b) and (c) show the overall view and cross section of array of parallel electrode system. Array of parallel grooves with a depth of about 0.5 mm was made on a poly (methyl methacrylate) (PMMA) substrate. The diameter of tungsten wire electrode fixed in the groove was 0.06 mm. Then the surface of the PMMA substrate was covered by a very thin plastic film (Parafilm, Pechiney Plastic Packaging Company). The distance between two adjacent electrodes was 1 cm. Spaced wire electrodes were connected to ground and AC voltage source, respectively. Expected advantages of the proposed electrode array are, 1) MWCNT/epoxy mixture between each electrode pair is not physically separated by electrode, thus the electrical connection is encouraged to form between adjoining parts; 2) UV-cured composite film on the Parafilm is easy to be peeled off; 3) The maximum electric filed near the wire surface is moderated so that CNTs is suppressed to be trapped near the wire by positive dielectrophoresis. MWCNTs (0.05 wt.%) /UV-curing epoxy mixture was thinly spreaded on the Parafilm. AC 5 kV, 4 kHz was applied on the wire electrodes for 10 min, and then cured by UV lamp.

C. Optical observation and electrical characterization of the composite film

The cured MWCNT/epoxy composite film was cut into 1.5×1.5 cm^2 for resistance measurement. The DC resistance and anisotropic properties of the square sample was measured by two probes method using ultrahigh resistance meter (Advanced R8340, Japan) under a constant condition of 25°C and 10% humidity. DC 1 kV was applied on two opposite sides of square sample. The conductive paste was covered on cross section to make sure that copper wire electrodes contact well with the film. The anisotropy of electrical properties was characterized by measuring the resistance both parallel and vertical to the direction of applied electric field. An optical microscope (Keyence R8340, Japan) was used to observe the MWCNTs network.

III. Results and Discussion

A. Effects of applied electric field time

In order to investigate the effect of applied electric field time on the course of conductive network formation, AC high electric field of 2 kV/cm with frequency at 4 kHz was applied on 0.05 wt.% well dispersed pristine MWCNT/epoxy mixture for various duration, which was followed by UV curing. Due to the rapid UV induced curing of the epoxy resin, the alignment of MWCNTs was effectively preserved in epoxy after the electric field removal. As a control sample, the same mixture without applying electric field was also prepared which stand for 0 min. Different morphology of aligned MWCNTs networks were showed as macroscopic images in Fig. 2 (a1)-(a4) and microscopic images in Fig. 2 (b1)-(b4). It was found that MWCNTs were aligned in the direction of the applied electric field. The degree of orientation and alignment became high as the application duration of electric filed became longer. Fig.3 shows DC resistivity of each sample, which was measured along two directions (parallel or vertical to electric field). As expected

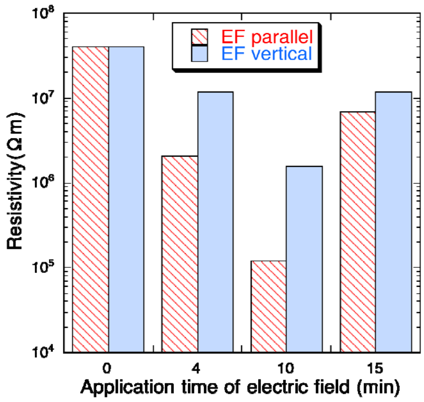

Figure 2. Anisotropy DC resistivity of aligned MWCNT/epoxy composites film as a function of applied electric field time.

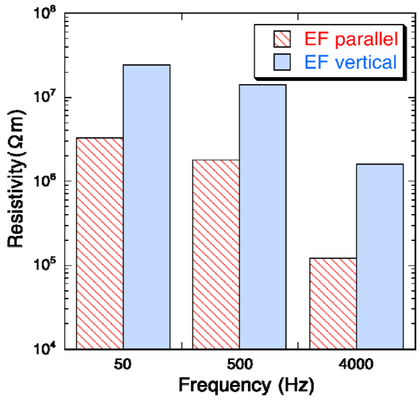

Figure 3. Anisotropy DC resistivity of aligned MWCNT/epoxy composites film as a function of frequency of electric field.

from CNT orientation along the electric field direction showed in Fig. 2 (b2)-(b4), samples obtained under AC electric field shown the anisotropic resistivity. The resistivity decreased to 1.21×10^5 Ωm and 1.58×10^6 Ωm in the direction of parallel and vertical to electric field when electric field was applied for 10min. In contrast, the sample without applying electric field has a uniform resistivity of 4×10^7 Ωm as a result of randomly dispersed MWCNTs. The decreased and anisotropic resistivity could be attributed to the formation of conductive network, which was mainly aligned along the electric field direction. It is interesting to note that when electric field application time was shorter than 10min, the differences of resistivity in parallel and vertical directions became larger, while the resistivity in both two directions decreased. This may be caused by intersection of aligned MWCNTs so that the current could flow easily through the cross region in the perpendicular direction. However, the resistivity increased and anisotropy was lost when electric field was applied for 15 min or much longer time. This may be explained by low density of aligned MWCNTs between electrodes while more MWCNTs deposited at the edge of electrodes. In Fig.2 (a4), it can be observed that upper and lower sides of the film, where the plane electrodes exist, looks darker than middle of the electrode gap, showing that more CNTs are trapped to the electrodes. We also observed that most of MWCNTs moved to the edge of electrodes when applied electric field was applied for 30 min. According to the mechanism of AC electric field induced alignment, the dielectrophoreis (DEP) force drives MWCNTs to move toward regions of high electric field and thereby to be deposited near the electrodes. These results suggest that the resistivity of MWCNT/epoxy composites film is greatly affected by the status of aligned network induced by electric field.

B. Effect of electric field frequency

50 Hz, 500 Hz and 4 kHz AC electric field of 2 kV/cm was applied on 0.05 wt.% well dispersed MWCNT/epoxy mixture for 10min respectively. Figure 4 shows the resistivity of cured pristine MWCNT/epoxy composites film as a function of frequency of electric field. It can be seen that the resistivity decreased with increasing the frequency. Kumar et al. reported that the tangled nanotubes are straightened with increasing frequency as the ac electric field exerts alternating force on both ends of the tubes at a higher speed so that the nanotubes adjust themselves and aligned more parallel to the direction of electric field [18]. In this study, as the carbon nanotube is nano-sized material, optical microscopy may not adequate to observe the concrete degree of orientation. However, a low resistivity of 10^5 Ωm in the direction of aligned MWCNT was reached at 4 kHz, which meant that carbon nanotubes well aligned and formed favorable conductive network in case of high frequency electric field. Therefore, it can be concluded that the nanotube alignment is strongly dependent on the frequency of the applied electric field.

C. Large scale film

Symmetrical wire electrodes were used to attain uniform electric field between each electrode pair. The electric field distribution was calculated using a COMSOL multiphysics software. The relative dielectric constant of uncured epoxy resin is 120 [23]. According to the designed electrode system, the model was created as shown in Fig. 5(b). Figure 5(a) shows the norm of electric field distribution of system. Figure 5(c) shows the x-component of electric field in resin along with x-axis. The electric field between each pair of wire electrodes has a little difference with each other because of the effect of compound electric field, but it can be seen that proximate uniform electric field was generated between each electrode pair. The simulation result was consistent with our intention. The electric field in parallel direction (x-component) mainly affords the momentum for alignment of MWCNTs. Using the array of parallel electrodes, it is desired to form conductive network by this alignment of MWCNTs.

The practicality of MWCNT/epoxy film was fabricated as large as 5×5 cm^2 in square. The images of film prepared by applying high electric field are shown in Fig. 6 (a) and (b). It was observed that MWCNTs aligned and formed conductive network between each pair of the electrodes along the direction of electric field. It is noticed that the area near wire electrodes had lighter color than mid-gap area, suggesting that less CNTs existed near wire electrodes. In order to investigate how CNTs distribution and alignment affect the film resistivity, the large film was cut into two sizes of square for resistivity measurement. One was 1.0×1.0 cm^2, which was selected from the space between electrode pair (Sample A). The other one was 1.5×1.5 cm^2, which included the area on top of a wire electrode (Sample B). Two samples of each size were measured and the average was taken to estimate the uniformity of conductive properties.

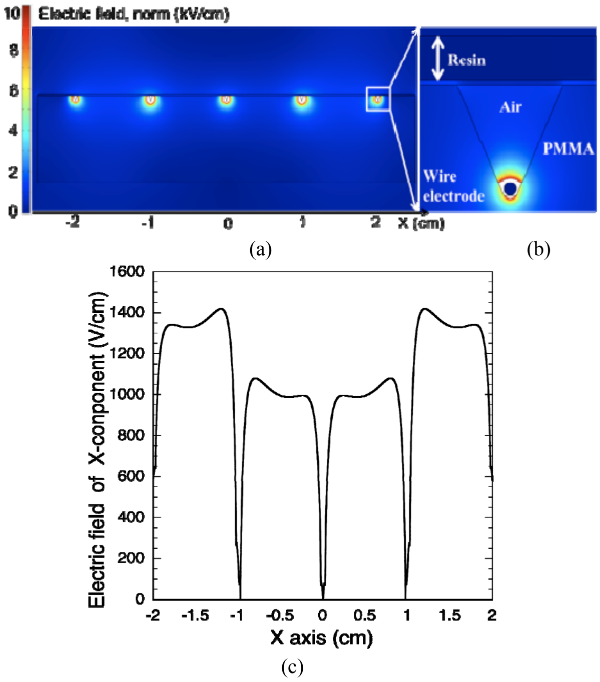

Figure 4. (a)Simulation of electric field distribution created by array of paralle electrodes. (b)Amplification of simulation model. (c) Electric field of X-component in epoxy resin.

Table 1 shows the results of resistivity measurement. The average resistivity of Sample A decreased to 1.08×10^5 Ωm and 1.85×10^6 Ωm in the direction of parallel and vertical to the electric field. The average resistivity of Sample B was 3.95×10^6 Ωm and 1.29×10^7 Ωm in the direction of parallel and vertical to the electric field, respectively. Considering that a composite film made of the same components without applying the electric field (Sample C) had a uniform resistivity of 1.17×10^8 Ωm, it was concluded that the lower resistivity was obtained by applying ac electric field using the proposed electrode array. For both sample A and B, the resistivity measured along electric field direction was almost one order of magnitude lower than that in vertical direction, showing anisotropic resistivity, which was

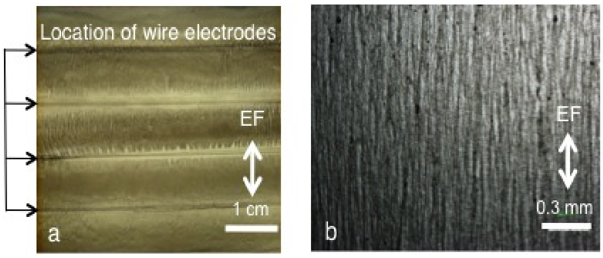

Figure 6. (a) Macroscopic images and (b) Microscopic images of film formed by applying electric field using array of parallel wire electrodes.

TABLE I. THE RESISTIVITY OF FILM PREPARED BY APPLYING ELECTRIC FIELD AND WITHOUT APPLYING ELECTRIC FIELD.

Sample	**Position**	**Average resistivity (Ωm)**	
		Parallel to electric field	***Vertical to electric field***
A	Between wire electrodes	1.08×10^5	1.85×10^6
B	Across wire electrodes	3.95×10^6	1.29×10^7
C	No electric field	1.17×10^7	

obtained by one pair of parallel electrodes. It could be attributed to the formation of conductive network which was mainly aligned along the electric field direction as shown in Fig.6. However, the conductive properties of film on top of wire electrode (Sample B) was not better than that of the film between electrodes (Sample A). From the electric field simulation result, it can be known that there is a narrow area on top of wire electrode where the electric field of x-component is weak. It may cause that MWCNTs moved to high electric field so that the conductive network did not formed so well on top of wire electrode. The defect of conductive pathway affected the uniformity of the whole film. So the detail of electrode arrangement should be improved further.

By using array of parallel electrodes, any size of film can be made readily. Because the voltage has to be increased to enlarge the gap distance of typical parallel electrodes to prepare large scale film. There is a limitation of practicability. In contrast, this new type of array of parallel electrodes overcame the disadvantage mentioned above. The size of film only depends on the quantities of wire electrode.

IV. CONCLUSION

In summary, macro-scale network of MWCNTs formed in UV cured epoxy by applying AC high electric field. The resistivity of 0.05 wt.% pristine MWCNT/epoxy composites film reached approximately 10^5 Ωm in parallel direction to the MWCNTs alignment, which decreased about three orders of magnitude than that of without electric filed application. High frequency electric field was possible to improve the alignment of CNTs and conductive properties.

The large scale MWCNT/epoxy conductive composite film was prepared by using array of parallel electrodes. The array of parallel electrodes system used in this work offers several advantages over the typical parallel electrodes: 1) No need for high voltage to maintain the same electric field when adding the quantity of electrode; 2) The process is simple and easy for practical application. Although some improvements in uniformity of conductivity are required in future, very large scale film (in principle completely accessible) can be fabricated by using proposed array of parallel electrodes.

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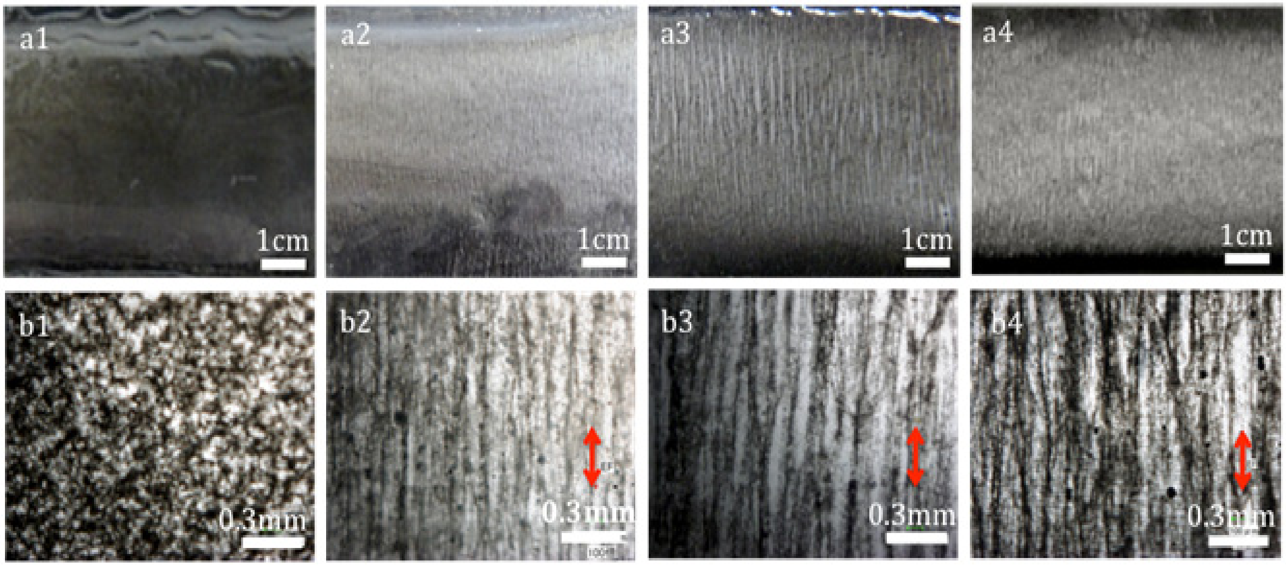

Figure 2. The MWCNTs in the cured epoxy resin. (a)Macroscopic images (b) Microscopic images of 0.05 wt.% MWCNTs network formed by applying Electric field for (1) 0 min. (2) 4 min. (3) 10 min. (4) 15 min. The arrows indicated the direction of AC electric field.