Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Improvement of Electrical Property in Laterally Aligned CNT/Polyaniline Composite Thin Film by Rubbing Technique

Hiroyuki Nakamatsu [a], Eiji Itoh [a] & Keiichi Miyairi [a]

[a] Department of Electrical and Electronic Engineering, Shinshu University, Wakasato, Nagano, Japan

Version of record first published: 22 Sep 2010

To cite this article: Hiroyuki Nakamatsu, Eiji Itoh & Keiichi Miyairi (2007): Improvement of Electrical Property in Laterally Aligned CNT/Polyaniline Composite Thin Film by Rubbing Technique, Molecular Crystals and Liquid Crystals, 472:1, 95/[485]-103/[493]

To link to this article: http://dx.doi.org/10.1080/15421400701545163

Mol. Cryst. Liq. Cryst., Vol. 472, pp. 95/[485]–103/[493], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701545163

Improvement of Electrical Property in Laterally Aligned CNT/Polyaniline Composite Thin Film by Rubbing Technique

Hiroyuki Nakamatsu
Eiji Itoh
Keiichi Miyairi
Department of Electrical and Electronic Engineering,
Shinshu University, Wakasato, Nagano, Japan

We have investigated the electrical property of carbon nanotube (CNT)/Polyaniline (PANI) composite thin film. It was found that the electrical conductivity of CNT/PANI composite film increases by seven orders of magnitude with the increment of functionalized SWCNT loading from 0 to 20 wt%, whereas little change was observed in pristine MWCNT/PANI composite. The electrical conductivity of the composite increases by conventional rubbing technique in the rubbing direction successfully. The increment of electrical conductivity in rubbed composite film strongly depends on SWCNT loading The electrical conductivity of rubbed composite film doped with 20 wt% functionalized SWCNT increases by factor of ~12 compared to the non-rubbed film, which is considered as an unique technique to control the anisotropy of electrical conductivity in the aligned conjugated polymer/CNT composite.

Keywords: anisotropy of electrical conductivity; carbon nanotube; composite; polyaniline; rubbing

1. INTRODUCTION

Carbon nanotubes (CNTs) has been attracting a great deal of attention recently because of their excellent thermal stability, unique mechanical and electronic properties, such as very high aspect ratio, high thermal and electrical conductivity [1–4]. The CNT/polymer composites dispersed in the solution processable polymer binder should therefore

This work was supported by the CLUSTER of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Address correspondence to Eiji Itoh, Department of Electrical and Electronic Engineering, Shinshu University, 4-17-1 Wakasato, Nagano, Japan. E-mail: eitoh@shinshu-u.ac.jp

have the potential of various applications such as electrostatic dissipation, electromagnetic interference (EMI) shielding, electrode material for the printable circuit, printable field effect transistors, and transparent conductive coatings [5–9]. Polyaniline (PANI) is one of the most promising conducting polymers because of its relatively chemical and thermal stability, low cost and easy film preparation, but its conductivity can be reversibly controlled with the conjugated backbone or by protonation of the nitrogen [10]. Therefore several reports has been reported about the enhanced conductivity of CNT/PANI composite with a low percolation threshold [11–14]. The electrical properties of the composites parallel to the substrate will be further improved if the direction of CNTs is controlled in the plane parallel to the substrate. There are some reports on the vertical aligned nanotubes by using high magnetic fields and fibers of aligned nanotubes by using the electrophoresis [15,16]. However, there are little reports on the electrical properties of CNTs film aligned parallel to the substrate in the lateral direction probably due to the difficulty of CNT dispersion in the conducting polymer binder and the difficulty of the application of very high external electric (or magnetic) field in the direction parallel to the substrate. On the other hand, it is well known that rubbing of the thin polymer surface is one of the typical techniques for the surface alignment of polymeric materials and widely used for the alignment of liquid crystals deposited on the aligned polymer surface.

In this study, we investigated the electrical conductivity of functionalized SWCNT/PANI composite and pristine MWCNT/PANI composite as a function of CNT concentration by weight. We also investigated the electrical conductivity change of the aligned ultra thin CNT/PANI composite. We then demonstrated the rubbing effect on the electrical properties of the composite film.

2. EXPERIMENTAL

Two types of carbon nanotubes, single-walled carbon nanotubes functionalized with carboxylic acid (SWCNT-COOH) with a purity of ca. 85–90% and pristine multi-walled carbon nanotubes (MWCNT) with a purity of >90% were used in this study. Here, the diameter of SWCNT-COOH and MWCNT is 4–5 nm and 20–30 nm and the length of the nanotubes are 0.5–1.5 μm and 0.5–2 μm, respectively. Firstly, CNTs were ultra-sonicated in 1-Methyl-2-pyrrolidinone (NMP) for 3 h to obtain the dispersion of MWCNT and to dissolve SWCNT-COOH in NMP, respectively. Here, the density of CNTs was 4 g/l. Leucoemeraldine base polyaniline (PANI) solution with a

density of 40 g/l in NMP was then mixed with the solution or dispersion of CNTs followed by the second ultra-sonication for 10 min to obtain the uniform dispersion of CNT/PANI composite.

A 30 nm-thick CNT/PANI composite film were then prepared by spin-coating technique on a glass slide with several pairs of 2 mm-wide collinear gold stripes with the gap of 90 μm in length. Subsequently, the spincoated films were then heat-treated on a hot plate at 120°C for 20 min.

The films of the surfaces were then rubbed by velvet film (YA-20-R: Yoshikawa chemical) which is reeled around the rotating roller with a diameter of 25 mm and the rotating speed of the roller was controlled between 2000 rpm and 9000 rpm. We prepared three types of films, without rubbing, rubbed in a direction parallel to the collinear electrodes across the gap, and rubbed in a direction vertical to the collinear electrodes.

The electrical property of composite was measured in an evacuated atmosphere ($\sim 10^{-2}$ Torr) by using an electrometer (KEITHLEY6517A). And scanning electron micrographs of surface of CNT/PANI composites coated by a sputtered 10-nm thick Au thin film were measured by using a JEOL JSM-7000F scanning electronic microscope (SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of SWCNT-COOH/PANI and MWCNT/PANI composites as a function of CNT concentration by wt%. The conductivity of non-doped PANI film is relatively very low as $\sim 10^{-9}$ S/cm and it increases with the increment of SWCNT-COOH loading and it becomes as high as 0.007 S/cm in 20 wt%-SWCNT-COOH doped PANI film. That is, the electrical conductivity of SWCNT-COOH doped PANI increases by a factor of 10^7 by 20 wt% CNT loading. The inset in Figure 1 shows the change in the conductivity in a low SWCNT-COOH loading. From this figure, the percolation threshold is 1.5 wt%.

On the other hand, the conductivity of pristine MWCNT/PANI composite does not improved at all compared to the SWCNT-COOH doped film.

Figures 2(a) and (b) shows the SEM images of SWCNT-COOH (30 wt%)/PANI composite and Figures 2(c) and (d) shows the SEM images of MWCNT/PANI composite, respectively. High-resolution scanning electron microscopy analysis reveals the presence of randomly networked SWCNTs but aligned laterally in the substrate plane. The diameter of SWCNT-COOH wires observed in Figure 2(a) was $\sim$20 nm, which is wider than the diameter of SWCNT-COOH,

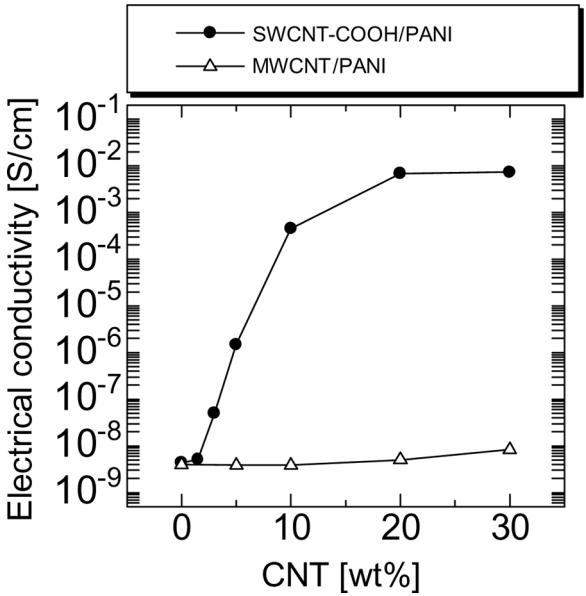

FIGURE 1 The electrical conductivity of SWCNT-COOH/PANI and MWCNT/PANI composites as a function of CNT concentration by wt%.

$\sim$5 nm, suggests the aggregation of CNTs. It should be noted here, however, that the SEM images of CNTs coated by different thickness of Au gives different diameters. We therefore considered that each SWCNT-COOH separates each other in the polymer matrix successfully. On the other hand, the SEM images of MWCNT (30 wt%)/PANI composite reveals that MWCNTs tangle each other and the large domain like island structure is clearly observed instead of uniform dispersion of CNTs. It is therefore revealed from Figures 1 and 2 that the uniformly dispersion of SWCNT network in the SWCNT-COOH/PANI composite improve the electrical conductivity drastically, whereas the separation of island like CNT domain in the MWCNT/PANI composite does not improve the electrical conductivity at all. That is, a smooth sidewalls of pristine CNT surfaces are incompatible with the solvent and PANI resulting in poor dispersion of nanotubes in the polymer matrix, whereas a homogeneous network of carbon nanotubes is obtained successfully by the use of noncovalently functionalized CNT surfaces. The electrical conductivity of SWCNT-COOH/PANI composites is, however, still very small compared to that of pure SWCNTs, $>10^3$ S/cm [4], probably due to the large contact and inter-nanotube resistance of PANI between each CNT wires.

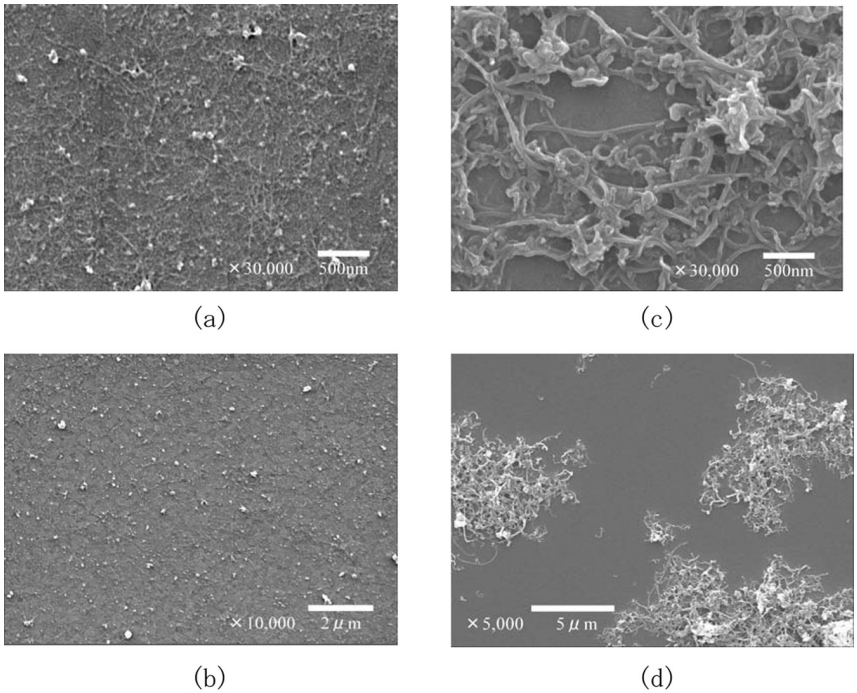

FIGURE 2 The SEM images of (a) SWCNT-COOH (30 wt%)/PANI composite (×30,000), (b) (×10,000), (c) Pristine MWCNT (30 wt%)/PANI composite (×30,000), and (d) (×5,000).

The re-arrangement of CNTs seems to be an efficient procedure to improve these problems.

We have then investigated the rubbing condition of CNT/PANI composites to optimize the conducting network. Figure 3 shows the relationship between the rotation speed of velvet films and the electrical conductivity of SWCNT-COOH (20 wt%)/PANI composite ultra thin film (ca. 30 nm) in the direction parallel to the rubbing direction. The conductivity of rubbed film clearly increases between 2000 rpm and 6000 rpm, and it decreases with the rotation speed above 7000 rpm. Figure 4 show the relationship between the concentration of SWCNT-COOH and the electrical conductivity of as-deposited SWCNT-COOH/PANI composite σ_0, the rubbed composite in the direction parallel to the rubbing direction $\sigma_{\parallel}$, and the rubbed composite vertical to the rubbing direction $\sigma_{\perp}$, respectively. The rotation speed of the rubbing was 5000 rpm. The conductivity of the film

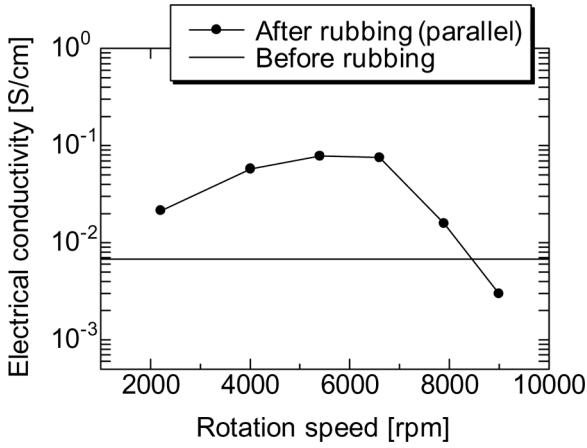

FIGURE 3 The relationship between the rotation speed of velvet films and the electrical conductivity of SWCNT-COOH (20 wt%)/PANI composite ultra thin film (ca. 30 nm) in the direction parallel to the rubbing direction.

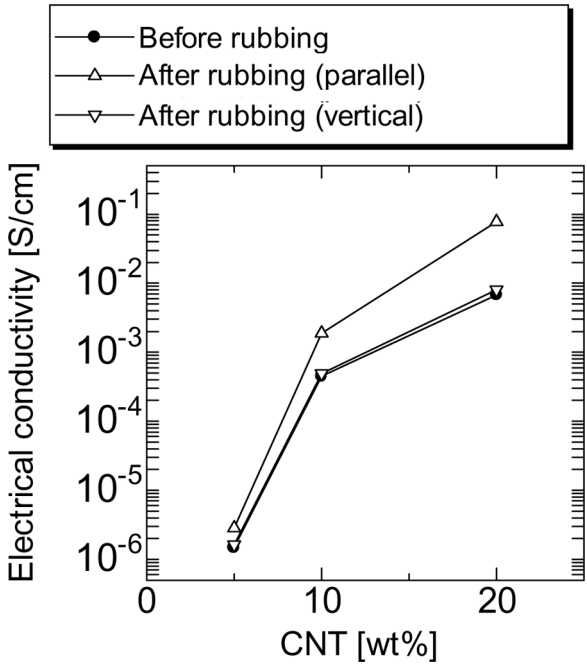

FIGURE 4 The relationship between the concentration of SWCNT-COOH and the electrical conductivity of as-deposited SWCNT-COOH/PANI composite σ_0, the rubbed composite in the direction parallel to the rubbing direction $\sigma_{\|}$, and the rubbed composite vertical to the rubbing direction $\sigma_{\perp}$, respectively.

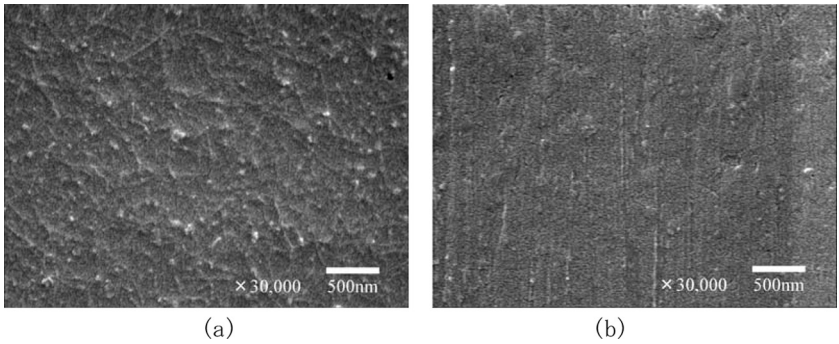

FIGURE 5 The SEM images of SWCNT (30 wt%)/PANI composite ultra thin film of (a) before and (b) after rubbing treatment.

rubbed in the parallel direction increases remarkably, whereas the electrical conductivity changes little in the film rubbed vertically. It should be noted here that the ratio of the conductivity of non-rubbed

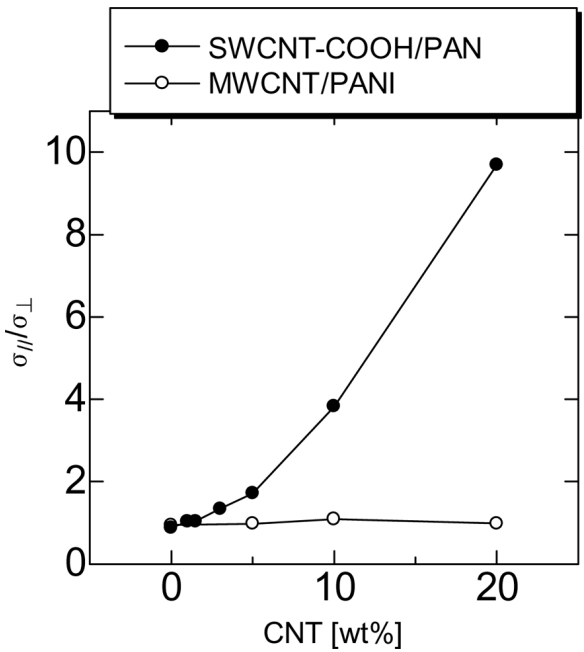

FIGURE 6 The relationship between the CNT concentration and the anisotropy of electrical conductivity, $\sigma_{\parallel}/\sigma_{\perp}$, of rubbed SWCNT/PANI composite and MWCNT/PANI composite as a function of the CNT concentration.

film to rubbed film, defined as $\sigma_{\parallel}/\sigma_0$, does not change at all in pure PANI film. On the other hand, $\sigma_{\parallel}/\sigma_0$ increases with the concentration of SWCNTs and it increases by factor of 12 at 20 wt%. That is, the re-arrangement of SWCNTs in the polymer network is probably a dominant factor of conductivity change. Figure 5 shows the SEM images of SWCNT (30 wt%)/PANI composite ultra thin film before and after rubbing treatment. The difference in the SEM images strongly supports that a randomly aligned SWCNT network is rearranged parallel to the rubbing direction resulting to the increment of the electrical conductivity. Figure 6 shows the relationship between the CNT concentration and the anisotropy of electrical conductivity, $\sigma_{\parallel}/\sigma_{\perp}$, of rubbed SWCNT/PANI composite and MWCNT/PANI composite as a function of the CNT concentration. The anisotropy of electrical conductivity increases with CNT concentration above percolation threshold and it increases by factor of 10 at 20 wt%. We therefore concluded that the rubbing of the uniformly dispersed CNT in the polymer network is an easy and effective way of controlling the unique electrical properties of aligned CNT/conducting polymer composite thin film.

4. CONCLUSIONS

We investigated the electrical conductivity of carbon nanotube (CNT)/Polyaniline (PANI) composite thin film. An uniform and randomly aligned carbon nanotube network was successfully obtained by using the functionalized SWCNT/PANI composite, whereas the pristine MWCNT did not disperse in polymer network at all. The electrical conductivity of SWCNT/PANI composite film was controlled by factor of 10^7 by changing the concentration of functionalized SWCNT from 0 to 20 wt%. We have demonstrated an unique fabrication technique to control the electrical conductivity of SWCNT/PANI composite by conventional rubbing technique. The SEM images revealed that the electrical conductivity of the composite films increases in the rubbing direction by the rearrangement of CNTs in the polymer network. The increment of electrical conductivity in rubbed composite film also strongly depends on SWCNT concentration. The electrical conductivity of rubbed composite film doped with 20 wt% functionalized SWCNT increased by factor of $\sim$12 compared to the non-rubbed film. The anisotropy of electrical conductivity in the CNT/conducting polymer network is considered as an unique technique for the application of polymeric conducting film, such as aligned conjugated polymer/CNT composite.

REFERENCES

[1] Iijima, S. & Ichihashi, T. (1993). *Nature*, *363*, 603.
[2] Saito, R., Dresselhaus, G., & Dresselhaus, M. S. (1998). *Physical Properties of Carbon Nanotubes*, Imperical College Press: London.
[3] de Heer, W. A., Châtelain, A., & Ugarte, D. (1995). *Science*, *270*, 1179.
[4] Wu, Z., Chen, Z., Du, X., Loganl, J. M., Sippel, J., Nikolou, M., Kamaras, K., Reynolds, J. R., Tanner, D. B., Hebard, A. H., & Rinzler, A. G. (2004). *Science*, *305*, 1273.
[5] Kilbride, B. E., Coleman, J. N., Fraysse, J., Fournet, P., Cadek, M., Drury, A., Hutzler, S., Roth, S., & Blau, W. J. (2002). *J. Appl. Phys.*, *92*, 4024.
[6] Park, C., Ounaies, Z., Watson, K. A., Crooks, R. E., Smith, J., Jr., Lowther, S. E., Connel, J. W., Siochi, E. J., Harrison, J. S., & St. Clair, T. L. (2002). *Chem. Phys. Lett.*, *364*, 303.
[7] Barraza, H. J., Pompeo, F., O'Rear, E. A., & Resasco, D. E. (2002). *Nano Lett.*, *2*, 797.
[8] Bo, X. Z., Lee, C. Y., Strano, M. S., Goldfinger, M., Nuckolls, C., & Blanchet, G. B. (2005). *Appl. Phys. Lett.*, *86*, 182102.
[9] Blanchet, G. B., Fincher, C. R., & Gao, F. (2003). *Appl. Phys. Lett.*, *82*, 1290.
[10] Chiang, J. C. & MacDiarmid, A. G. (1986). *Synth. Met.*, *13*, 193.
[11] Blanchet, G. B., Fincher, C. R., & Gao, F. (2003). *Appl. Phys. Lett.*, *82*, 1290.
[12] Ramasubramaniam, R., Chen, J., & Liu, H. Y. (2003). *Appl. Phys. Lett.*, *83*, 2928.
[13] Blanchet, G. B., Subramoney, S., Bailey, R. K., Jaycox, G. D., & Nuckolls, C. (2004). *Appl. Phys. Lett.*, *85*, 828.
[14] Long, Y., Chen, Z., Zhang, X., Zhang, J., & Liu, Z. (2004). *Appl. Phys. Lett.*, *85*, 1796.
[15] Smith, B. W., Benes, Z., Luzzi, D. E., Fischer, J. E., Walters, D. A., Casavant, M. J., Schmidt, J., & Smalley, R. E. (2000). *Appl. Phys. Lett.*, *77*, 663.
[16] Gommans, H. H., Alldredge, J. W., Tashiro, H., Park, J., Magnuson, J., & Rinzler, A. G. (2000). *J. Appl. Phys.*, *88*, 2509.