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Preparation of Honeycomb-patterned Polyaniline-MWCNT/Polystyrene Composite Film and Studies on DC Conductivity

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Conductive honeycomb-patterned polystyrene (PS) thin films were prepared by the formation of a polyaniline (PANI) thin layer on the surface of the patterned PS thin films using simple one-step chemical oxidative polymerization of aniline. The *in situ* chemical oxidation polymerization of aniline hydrochloride solution on the patterned structure of the PS films was conducted in the presence of multiwalled carbon nanotubes (MWCNT) to prepare the PANI-MWCNT/PS composite film. The concentration (wt %) of MWCNT was varied in the range of 1%-3% by weight. The dependence of surface morphology of the PANI/PS and PANI-MWCNT/PS composite film to the polymerization time was observed by scanning electron microscopy. The room temperature DC conductivity was obtained by the four-probe technique. The conductivity of the PANI-MWCNT/PS composite film was affected both by the MWCNT concentration and polymerization time. In addition, DC electrical field was loaded during the oxidative polymerization to affect the distribution of the MWCNT included in the composite film, varying the loading voltage in the range of 0.1-3.0 V. The conductivity of the PANI-MWCNT/PS composite film was increased as loading voltage rose. However, this increase stops at a voltage higher than the critical value.

Key Words : Carbon nanotubes, Composite materials, Conducting polymers, Honeycomb-patterned film

Introduction

Carbon nanotubes (CNTs) with unique structures and properties are attractive building blocks for novel materials and devices of important practical applications.[1] Composites based on polymers and nanotubes offer the possibility of obtaining materials with superior properties.[3] For the synthesis of composites based on polymers, conducting polymers (CPs) have been directed increasing attention because of their special features and potential applications in many fields including electromagnetic wave interference shielding, anti-static information storage and processing, sensor fabrication, and production of electrochromic materials.[4]

Among conducting polymers, PANI is the most promising material because of its low cost, ease of preparation, excellent environmental stability, and controllable physical and electrochemical properties such as oxidation and protonation. Progress in the development of an inexpensive signal processing system using micro and nanostructures have made the production of a variety of novel biomedical sensors possible.[5-7] There has been growing interest in research on the conducting polymer of PANI with nanostructures such as nanorods, nanotubes, nanowires, and nanofilms.[8-10] However, its application is restricted by its poor mechanical properties and low processability.

An efficient alternative is the preparation of PANI composites on porous polymer substrates, such as porous polypropylene,[11,12] cellulose acetate,[13] crosslinked polystyrene,[14,15] polyethylene[16-18] and polycarbonate.[19-21] In this approach, the polymer substrates provide good mechanical properties, and PANI acts as an active functional component. In this regard, preparing porous films is considered as a good candidate for preparing composites with PANI because their pores enable the formation of a continuous conducting network inside the carrier and decrease the reaction time of aniline polymerization. For instance, a PANI layer was obtained on the surface of microporous polyethylene films and the resultant composites had high conductivity and good mechanical properties.[17]

Recently, Lu *et al.* have reported the synthesis of polyaniline layers by simple one-step chemical oxidative polymerization based on the surface of a honeycomb-ordered porous polycarbonate film prepared *via* a water-assisted method.[22] Widawiski *et al.* firstly introduced the formation of honeycomb-patterned porous film using water-assisted method, in which highly ordered polymer films are produced by evaporating a solution of polymer dissolved in a volatile solvent under humid conditions.[23]

This method has been widely applied to the preparation of polymers with a highly regular porous array because of its simplicity, low cost, and dynamic control over the morphology of resultant pores.[24-27]

In the current paper, conductive honeycomb-patterned polystyrene (PS) thin films were prepared by the formation of a PANI thin layer on the surface of the patterned PS films by a simple one-step chemical oxidative polymerization of aniline in the presence of MWCNTs. PS films were used as a polymer matrix template because of their high transparency, low water absorbability, and good mechanical flexibility, in which the preparation of porous patterned-PS film was obtained by self-organization process *via* a water-assisted method. The PS solution was dissolved in chloroform solvent under humid conditions. The surface morphology and DC conductivity of the PANI-MWCNT/PS composite films depending on the oxidative polymerization time of aniline were observed by scanning electron microscopy (SEM) and the four-probe technique, respectively. The effect of DC electrical field for the arrangement of MWCNTs during the oxidative polymerization of aniline was also studied by loading electrical voltage in the range of 0.1-3.0 V.

Experimental

Materials. The PS standard (average molecular weight of 400,000 g mol^{-1}, Aldrich Co. product no. 330353), sulfuric acid (98%), nitric acid (65%), methanol (≥ 99.8%), aniline hydrochloride, ammonium persulfate, polyvinylpyrrolidone (average MW 40,000 g mol^{-1}), chloroform (99.8%), and pristine MWCNT (110-170 nm diameter and 5-9 nm length) were purchased from Aldrich company and used without further treatment, except the MWCNT.

Highly purified materials are necessary in applications that involve MWCNTs. However, the chemical inertness of graphitic networks presents a major challenge in composite material fabrication. The presence of oxygen-containing groups facilitates the exfoliation of CNT bundles and increases their solubility in polar media.[28,29] The chemical oxidation of the MWCNTs was carried out in a 3 to 1 mixture of concentrated H_2SO_4 and HNO_3 under sonication for 24 h at temperatures between 35 and 40 °C.[30] The remaining mixture was washed with DI water until pH 7 was obtained; the MWCNTs were collected by filtering and drying in a vacuum oven at 80 °C for 24 h. The treated MWCNTs obtained by this method were used in all the experimental processes.

Preparation of the Honeycomb-Patterned PS Thin Film as a Template. The procedure for the preparation of patterned PS thin films was introduced in a previous report.[31] A solution of PS in chloroform was cast on a glass Petri dish. An opaque film was obtained after complete evaporation of the solution in humid conditions. Evaporated water was applied on the solution surface through an air pump at a flow rate of 0.6 L/min to acquire a highly ordered honeycomb-patterned structure. The microporous film was formed *via* the condensation and deposition of water droplets on the solution surface resulting from evaporative cooling. The solution was cast onto a glass dish with a 30 mm diameter at 20 °C and 60% relative humidity.

Formation of the PANI Thin Layer on the Patterned PS Films. The patterned PS film was immersed in 0.325 M aniline hydrochloride solution. The polymerization of aniline to PANI was initiated by dropping 0.184 M ammonium persulfate solution into the aniline solution. The reaction

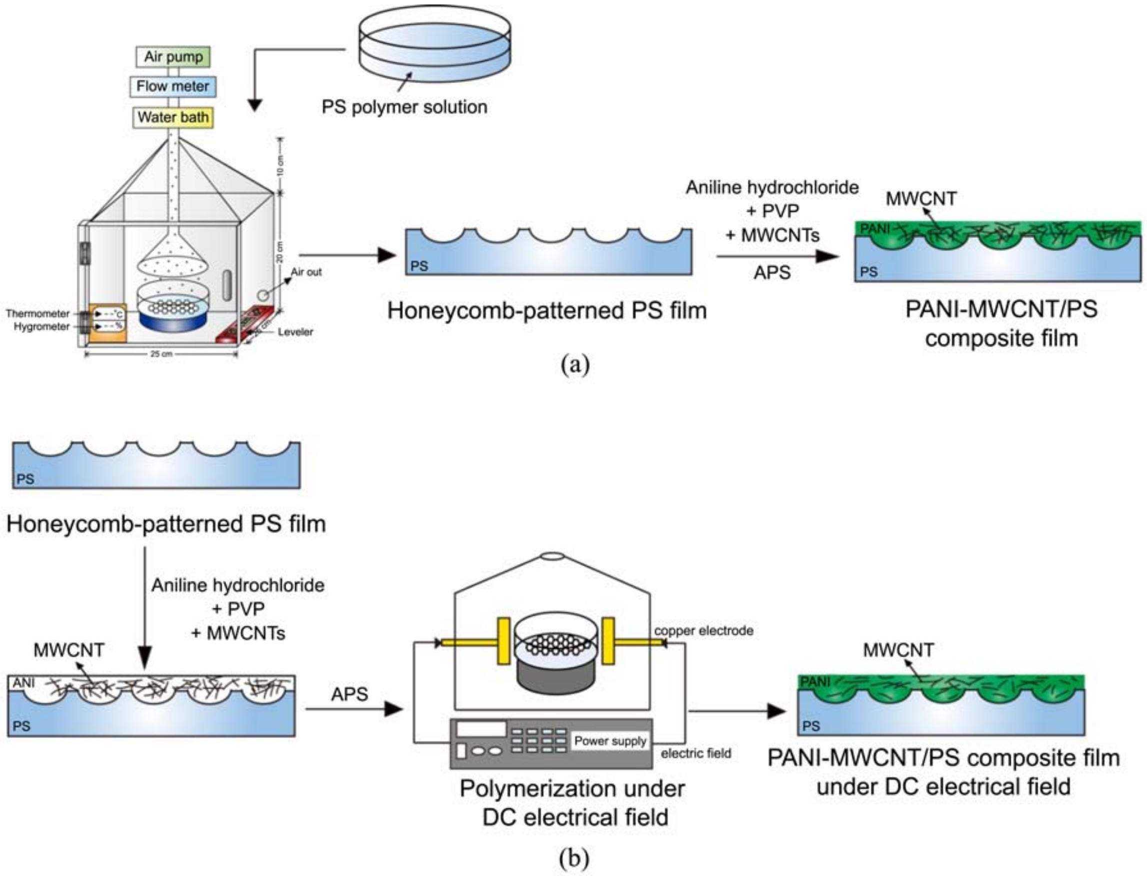


Figure 1. (a) Overall scheme for the formation of the PANI thin layer on the honeycomb-patterned PS film for the PANI-MWCNT/PS composite film, (b) the system for the formation of honeycomb-patterned PANI-MWCNT/PS composite film under DC electrical field.

was performed under ice-bath conditions varying reaction times from 1-8 h to observe the effect of polymerization time on the conductivity of the PANI/PS composite film. Subsequently, the film was washed with water, and the PANI/PS film was dried for 24 h at room temperature to observe surface morphology and conductivity.

The PANI-MWCNT/PS composite film was also prepared by a similar process. For the preparation of the composite films, different concentrations of MWCNT in the range of 1%-3% by weight were added into the 0.325 M aniline hydrochloride. The solution including MWCNTs was sonicated for about 5 h for well dispersion of MWCNT. Then, the patterned PS film was immersed in the solution containing MWCNT, and aniline polymerization was initiated by dropping 0.184 M APS solution. The reaction was performed under ice-bath conditions under several reaction times. The film was washed with water, and the PANI-MWCNT/PS composite film was dried for 24 h at room temperature. The overall reaction scheme for the formation of the patterned PANI-MWCNT/PS composite film is depicted in Figure 1(a).

The Effect of DC Electrical Field on the Formation of the PANI-MWCNT/PS Thin Layer. To study the effect of DC electrical field in the formation of the PANI-MWCNT/PS composite film, the MWCNTs in the aniline hydrochloride solution were loaded using the electrical field by the combination of a function generator (OR-X Co., Model No. 630) and voltage amplifier (AA Lab Systems, Model No. A-304). The DC voltage used for the loading was varied from 0.1 to 3.0 V. Figure 1(b) shows the summarized scheme for the preparation of the PANI-MWCNT/PS composite film obtained under DC electrical field.

Characterization of the PANI-MWCNT/PS Composite Film. The structures of surface morphology of the patterned PS template film, PANI/PS film, and PANI-MWCNT/PS composite thin film were observed using a scanning electron microscope (Coxem Co., Model NO. CX-100 s). The DC conductivity at room temperature for the PANI/PS and PANI-MWCNT/PS composite thin films was measured using the four-probe technique with a Keithly 224 constant current source and a Keithly 617 digital electrometer.

Results and Discussion

Preparation of the Honeycomb-Patterned PS Thin Film as a Template. Figure 2 shows a typical SEM image of a honeycomb-patterned PS template film, in which 2(a) shows the surface image and 2(b) shows the cross-sectional image. Highly ordered honeycomb-patterned PS films were obtained *via* the addition of an amphiphilic copolymer (P_1) to the 10 wt % PS solution. The copolymer was prepared by the copolymerization of dodecylacrylamide and 6-hexaamido acrylic acid.[33] For the preparation of the honeycomb-patterned PS film, the total amount of polymer used was kept constant at 0.25 g in 4 mL chloroform. The average pore diameter and pore height used for the patterned PS template corresponded to ~5 and ~4 μm, respectively.

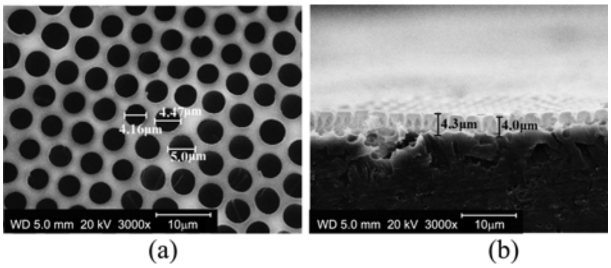
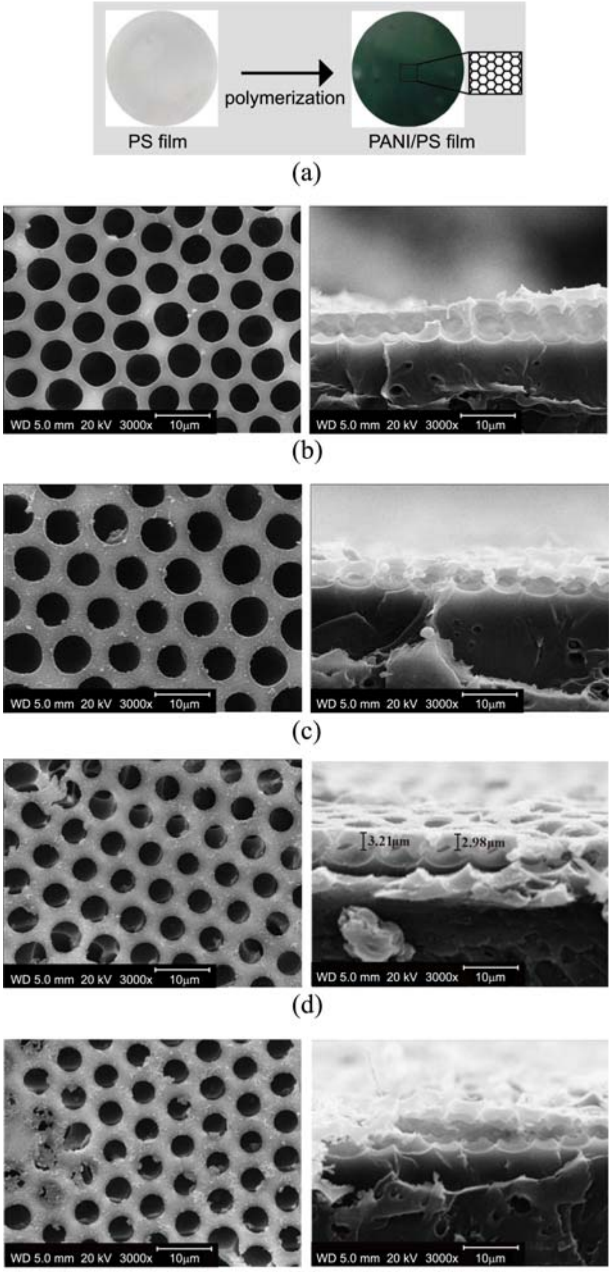


Figure 2. Typical SEM images of the honeycomb-patterned PS film used as a template for the PANI/PS film. (a) Surface image, (b) cross sectional image.

Formation of the PANI Thin Layer on the Patterned PS Films. Figure 3 shows the result for the formation of the PANI thin layer on the patterned PS films. Figure 3(a) shows the image of the color-changed PS template film by the polymerization of aniline with 2 h, taken using a digital camera (Sony DSC-W300). The change in film color from transparent to green clearly indicates the formation of the PANI layer on the honeycomb-patterned PS substrate because a green color is characteristic of the emeraldine form of conductive PANI.[22] Figures 3(b), 3(c), 3(d), and 3(e) show the typical SEM images for the formation of the PANI thin layer on the patterned PS film at polymerization times of 1, 2, 6, and 8 h, respectively. The polymerization was performed by immersing the patterned PS template film into the aniline hydrochloride solution and ammonium persulfate solution. A small amount of polyvinylpyrrolidone (PVP) (0.525 μmol) was added as a dispersing agent in the solution to facilitate well dispersion of PANI in the thin layer formation onto the PS template during the polymerization process. The water-soluble polymer of PVP is an effective material in particle dispersion because it protects the ultrafine particles from the coagulation caused by electric or steric repulsion between the absorption layers.[32] In this process, PVP was only added as a supporting material for the well-dispersion of polymerized polyaniline. The polymerization time of aniline was not affected at all by the addition of PVP regardless of the concentration of PVP. We have used the least amount of PVP because PVP is not conducting polymer.

The formation of the PANI thin layer on the surface of PS film is imperceptible at 1 h of polymerization as shown in Figure 3(b). At 2 h of polymerization, however, the formation of the PANI thin layer is signified by the appearance of nanosized spots as shown in Figure 3(c). The formation of the PANI thin layer on the surface of the PS film is clearly shown in Figures 3(d) and 3(e), at polymerization times of 6 and 8 h, respectively. The cross-sectional SEM images also confirm the formation of the PANI thin film on the surface of the patterned PS film. With the increase in polymerization time, the resultant thickness gradually increases as shown in the right-side images of Figures 3(b), 3(c), 3(d), and 3(e). The formation of the PANI thin film with an appropriate thickness was obtained at a 6 h polymerization, with an average coating thickness of 3 μm as shown in Figure 3(d).



(a) (b) (c) (d) (e)

Figure 3. SEM images showing the formation of the PANI thin layer on the surface of the patterned PS film. (a) Color change from transparent to green at 2 h polymerization of aniline on the surface of the PS film. The images of (b), (c), (d), and (e) show the effect of polymerization time for the formation of the PANI thin layer on the surface of the patterned PS film by increasing the polymerization time with 1, 2, 6, and 8 h, respectively.

However, an aggregated and insufficiently dispersed PANI layer was obtained at an excessive polymerization of 8 h as shown in Figure 3(e).

Formation of the Honeycomb-Patterned PANI-MWCNT/PS Composite Film. Figure 4 shows the SEM images of the honeycomb-patterned PANI-MWCNT/PS composite film, prepared by immersing the honeycomb-patterned PS film into the aniline hydrochloride/PVP solution containing MWCNTs. Figures 4(a), 4(b), and 4(c) show the typical SEM images with the degree of adsorption of MWCNTs in the PANI/PS film at polymerization times of 1, 2, and 8 h, respectively, when 1 wt % of MWCNT was dispersed in the aniline solution, while Figures 4(d), (e), and (f) show the SEM images obtained using 3 wt % of MWCNT under same polymerization time. In the case of Figures 4(a) and 4(b), the inclusion of MWCNTs on the PANI/PS film is not clearly observable because of short polymerization time of 1 h and 2 h, respectively. However, the formation of the PANI-MWCNT/PS composite film is clearly perceivable when the polymerization time of aniline solution containing MWCNT increases was increased to 8 h, as shown in Figure 4(c). The formation of the PANI-MWCNT/PS composite film is evident when the concentration of MWCNT was increased from 1 to 3 wt %, as shown in Figures 4(d), 4(e), and 4(f), in which aniline was polymerized by 1 h, 2 h, and 8 h, respectively. The figures show the formation of a network by the distributed MWCNTs in the PANI-MWCNT/PS composite film. Then, the formation of a distributed network by the added MWCNT in the PANI-MWCNT/PS composite film can act a role to increase the conductivity of the composite film. However, an aggregation of MWCNTs also appears as shown in Figure 4(f) under long polymerization time. This result indicates that long time of polymerization may cause the coagulation of MWCNTs in the PANI-MWCNT/PS composite film due to the electric or steric interaction between the absorption layers and interaction between MWCNT particles. This result well reflects the insolubility or poor dispersibility of pristine CNTs in common solvents, which acts as a serious obstacle to their further development. Therefore, various attempts have been made to obtain homogeneous CNT dispersions in both aqueous and organic media. Therefore, the added PVP in the polymerization of PANI could also act as a dispersing agent of MWCNTS in the PANI-MWCNT composite film formation.

Figure 5 shows the room temperature DC conductivity of the PANI/PS composite film depending on polymerization time and added MWCNT concentration. The conductivity of the pure PANI/PS film increases with polymerization time, however the conductivity is not so greatly increased by the polymerization time although the time was increased from 1 to 8 h. This result can be attributed to the fact that the thin layer of PANI on the PS surface forms at a comparatively short time (Figure 3). After this, further polymerization only increases the thickness of the PANI layer, which only causes the small increase of conductivity.

On the other hand, the figure shows that the conductivity of the PANI/PS films is greatly affected by the incorporation of MWCNT. The detailed observation shows that the concentration effect of MWCNT incorporated into the composite film is not so severe at a short polymerization time of up to 2 h. However, the conductivity considerably increases when MWCNT concentration and polymerization time increase. The results of the conductivity in the composite films suggest that MWNTs possesses a positive influence on the conducting property of the composites. This result is also

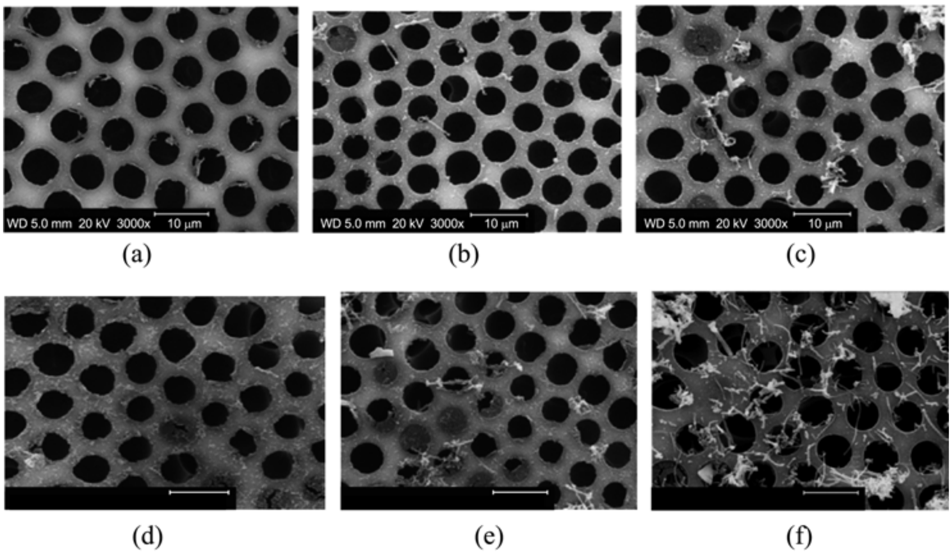


Figure 4. SEM images showing the formation of the PANI-MWCNT/PS composite film. The images of (a), (b), and (c) show the typical SEM images with the degree of adsorption of MWCNTs in the PANI/PS film at polymerization times of 1, 2, and 8 h, respectively when 1% (wt % to aniline) of MWCNT was dispersed in the aniline solution. The images of (d), (e), and (f) show the SEM images obtained using 3 wt % of MWCNT under same polymerization time.

consistent with the SEM images in Figure 4, in which the degree of incorporation of MWCNT into the composite film is insignificant at a short polymerization time. The DC conductivity depending on the concentration of added MWCNT is much higher when polymerization time exceeds 4 h as shown in Figure 5.

Effect of DC Electrical Field on the Formation of the PANI-MWCNT/PS Composite Film. In order to maximize the effect of incorporation of MWCNT on the conductivity of the PANI/PS film, the effect of DC electrical field during the preparation of the PANI-MWCNT/PS composite film was studied. This experiment was intended to protect the ultrafine particles from the coagulation caused by electric or steric repulsion between the absorption layers. Both sides of the Petri dish containing aniline hydrochloride solution with MWCNTs were loaded with an electrical field using a copper electrode (Figure 1(b)). The used DC voltage was varied from 0.1 to 3.0 V. Figures 6 shows the typical SEM images of the PANI-MWCNT/PS composite films prepared under DC electrical field. The image of the composite films shown in Figure 6 was obtained by loading 1.0 V. The concentration of MWCNT was 3%. In Figures 6, the images

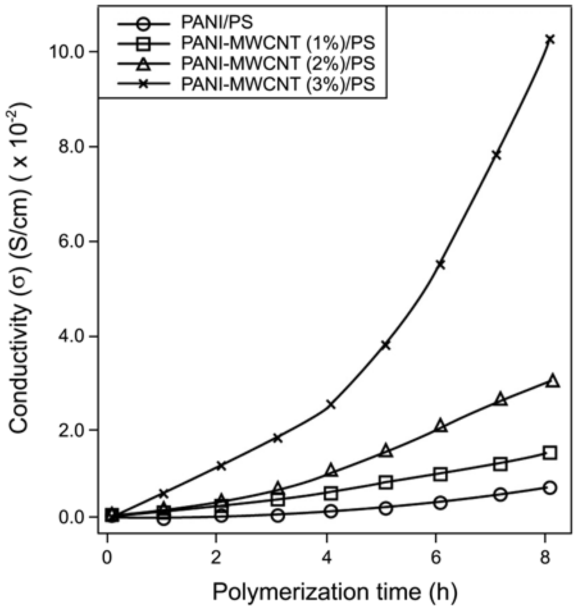


Figure 5. Room temperature DC conductivity depending on the time of polymerization and added MWCNT concentration (wt %).

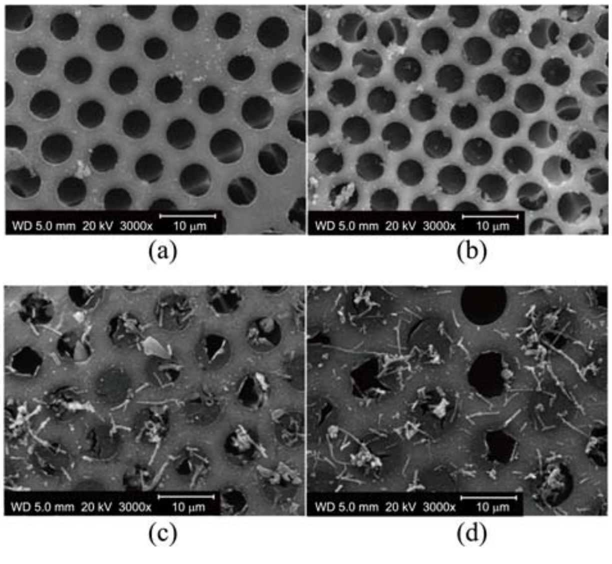


Figure 6. Typical SEM images showing the effect of loaded electrical field on the formation of the PANI-MWCNT/PS composite film obtained by the loaded voltage of 1.0 V. (a), (b), (c), and (d) show the SEM images of PANI-MWCNT/PS composite with the polymerization time of 1, 2, 6, and 8 h, respectively. 3 wt % of MWCNT was used.

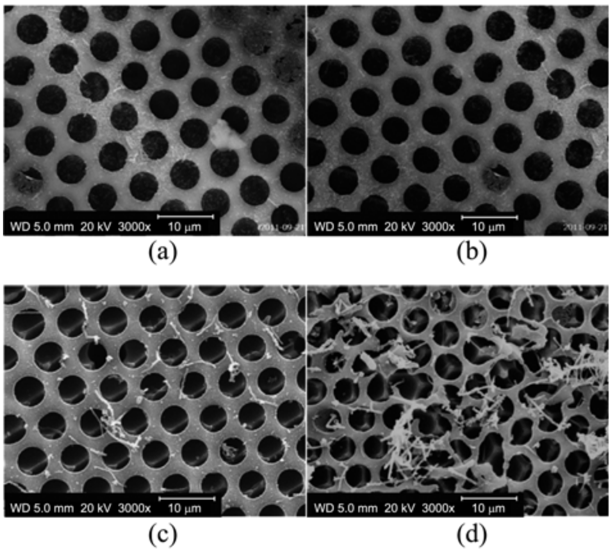


Figure 7. Typical SEM images showing the effect of loaded electrical field on the the formation of the PANI-MWCNT/PS composite film obtained by the loaded voltage of 3.0 V. (a), (b), (c), and (d) show the SEM images of PANI-MWCNT/PS composite with the polymerization time of 1, 2, 6, and 8 h, respectively.

in (a), (b), (c), and (d) indicate the dependence of the composite film on polymerization times of 1, 2, 6, and 8 h, respectively. The figure clearly shows that the DC electrical field has a positive effect on the dispersion of MWCNTs in the PANI-MWCNT/PS composite film. In particular, the comparison of Figure 4(f) (the image obtained by same condition with 3% and 8 h without the DC field) and Figure 6(d) visibly shows the role of the DC electrical field in the formation of the PANI-MWCNT/PS composite film. Figure 6(d) shows that the DC electrical field helps the dispersion of MWCNTs in the composite film without aggregation. However, the DC electrical field does not always exhibit a positive effect on the formation of the PANI-MWCNT/PS composite film. The higher loading voltage rather induced aggregation of in the composite film as shown in Figures 7(c) and 7(d) despite the polymerization times and concentrations being the same as those in Figure 6. This result indicates that overloading of the electrical voltage induces a negative effect on the dispersion of MWCNTs in the PANI-MWCNT/PS composite film, which can cause the MWCNTs in the composite film to coagulate with each other by inducing the electric or steric interaction between them. It is supported by the cross sectional images of the PANI-MWCNT/PS composite film depending on the loaded voltage. Figure 8(a) shows the image of PANI-MWCNT/PS composite film prepared without DC voltage using the polymerization time of 6 h, which shows the thickness of the film is not regular. However, the image shown in Figure 8(b) which was obtained by loading 1.0 V regular and modified surface, which indicates well dispersion of MWCNTs in the composite film. Figure 8(c) is the image obtained by loading 3.0 V, which shows irregular surface similarly to the Figure 8(a).

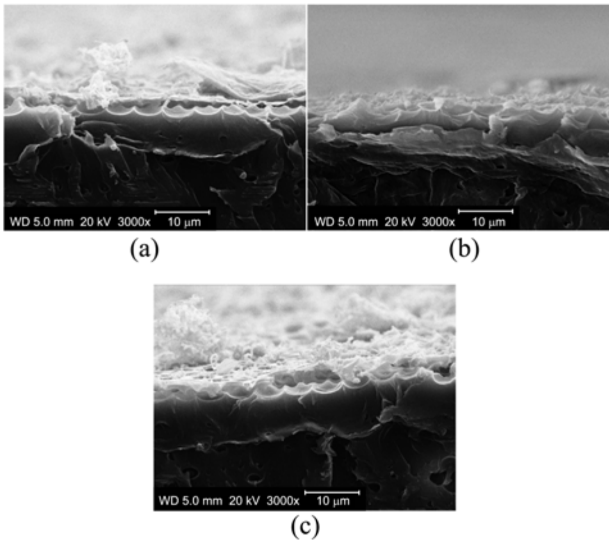


Figure 8. Cross sectional SEM images showing the effect of loaded electrical field on formation of the PANI-MWCNT/PS composite film. (a), (b), and (c) show the images obtained at the loaded voltage of 0 V, 1.0 V, and 3.0 V, respectively. For the PANI-MWCNT thin layer, 3 wt % MWCNT was used with 6 h polymerization.

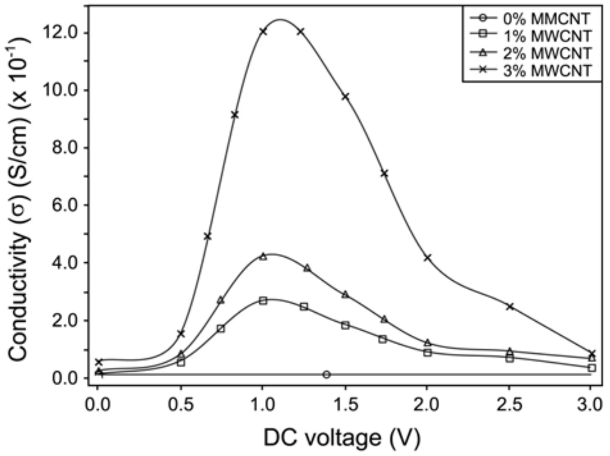


Figure 9. Room temperature DC conductivity depending on the loaded electrical field.

Figure 9 shows that the DC conductivity increases by increasing loaded voltage, but this increase is not linear by loaded voltage; the conductivity rather decreases with the increase in voltage at a level higher than a critical value regardless of the amount of incorporated MWCNT (1%, 2%, and 3%). This phenomenon is more evident at higher MWCNT concentration of 3% than 1%. This result can be attributed to the fact that the dense distribution of MWCNTs in the PANI-MWCNT/PS composite film can more easily be affected by the loaded voltage than can dilute distribution. Our experimental result shows that the critical voltage is nearly 1.0 V as shown in the figure. The conductivity increase by the dispersion of MWCNTs was rather not induced by the loaded voltage higher than 3 V.

Conclusion

We have prepared a honeycomb-patterned porous PANI/PS thin film through the formation of a PANI thin layer on the surface of patterned PS thin films *via* a simple one-step chemical oxidative polymerization of aniline. The *in situ* chemical oxidation polymerization of aniline hydrochloride solution on the patterned structure of the PS film was also conducted in the presence of MWCNTs to prepare the PANI-MWCNT/PS composite films, varying the wt % of MWCNT from 1% to 3% with and without loading the DC electrical field. The surface morphology and room temperature DC conductivities of the PANI-MWCNT/PS composite film depending on polymerization time, added MWCNT concentration, and loaded electrical voltage were studied. For the preparation of the PANI-MWCNT/PS composite film by the inclusion of MWCNTs during the formation of the PANI thin layer on the patterned PS, considerably more time was needed than for the formation of the pure PANI/PS thin film. The conductivity was increased by the increase of MWCNT concentration and the loading of DC electrical field also increased the conductivity in an appropriate voltage range.

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