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Template synthesis of conducting polyaniline composites based on honeycomb ordered polycarbonate film

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ABSTRACT

This paper describes the synthesis of polyaniline (PANI) layers by a simple one-step chemical oxidative polymerization, based on the surface of a honeycomb ordered porous polycarbonate (PC) film prepared *via* water-assisted method from PC/$CHCl_3$ solutions. The surface and cross-section morphology of the PANI/PC composite film was characterized by environmental scanning electron microscopy, indicating that the honeycomb ordered PC film plays the role as template in controlling the morphology of the PANI/PC composite film. The results of thermogravimetric analysis of the PANI/PC composite film showed higher thermal stability than PANI itself. The electrical conductivity of the PANI/PC composite film was also determined by the four-probe technique.

1. Introduction

Conductive polymer materials have attracted much attention because of their special features and potential applications in hi-tech aspects, such as the electromagnetic shielding, anti-static, information storage and processing, sensors, electrochromic materials, and so on. In the family of conducting polymers, polyaniline (PANI) is unique due to its electronic, thermoelectric, and optical properties as well as its good environmental stability. However, its application is restricted by the poor mechanical properties and low processibility.

To solve these problems, preparation of PANI composites on porous polymer substrate, such as porous polypropylene [1,2], cellulose acetate [3], crosslinked polystyrene [4,5], polyethylene [6–8] and polycarbonate [9–11], is an efficient alternative, where the polymer substrate provides good mechanical properties and PANI acts as an active component. In this method, it is usually believed that the most suitable materials for preparing composites with PANI are porous systems because their pores enable 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 micro-porous polyethylene films and the resultant composites had high conductivity and good mechanical properties [7].

Herein, the objective is to produce a conductive composite film with honeycomb ordered porous structure that maintains the mechanical properties, the processibility, and the thermal stability of conventional polymers, together with the electrical properties of conducting PANI. In our recent work, we have successfully fabricated conducting PANI/sulfonated polysulfone (SPSF) composite film with honeycomb porous structure by chemical oxidation polymerization of aniline, which was preorganized on the surface of SPSF film *via* electrostatic interaction [12]. Based on these results, it is interesting to attempt to prepare honeycomb ordered PANI composite films by *in situ* polymerization of aniline, which is first adsorbed on the surface of honeycomb porous substrate *via* weaker interaction, such as hydrogen bonding which is formed by the amino groups within aniline with the functional groups on the surface of honeycomb porous substrate. Further, the influence of preorganization of aniline on the surface of porous substrate *via* different interactions (electrostatic interaction or hydrogen bonding) on polymerization of aniline as well as the electrical conductivity of the resultant PANI composite film can be roughly compared, which should be worthful for obtaining PANI composite film with controllable morphology and electrical performance.

In this paper, the engineering plastic polycarbonate (PC) has been selected as a polymer matrix for its good mechanical strength, including high impact strength, good heat resistance, and good thermal stability. Bormashenko and co-workers [13,14] have reported the fabrication of regular patterned PC films by fast-dip

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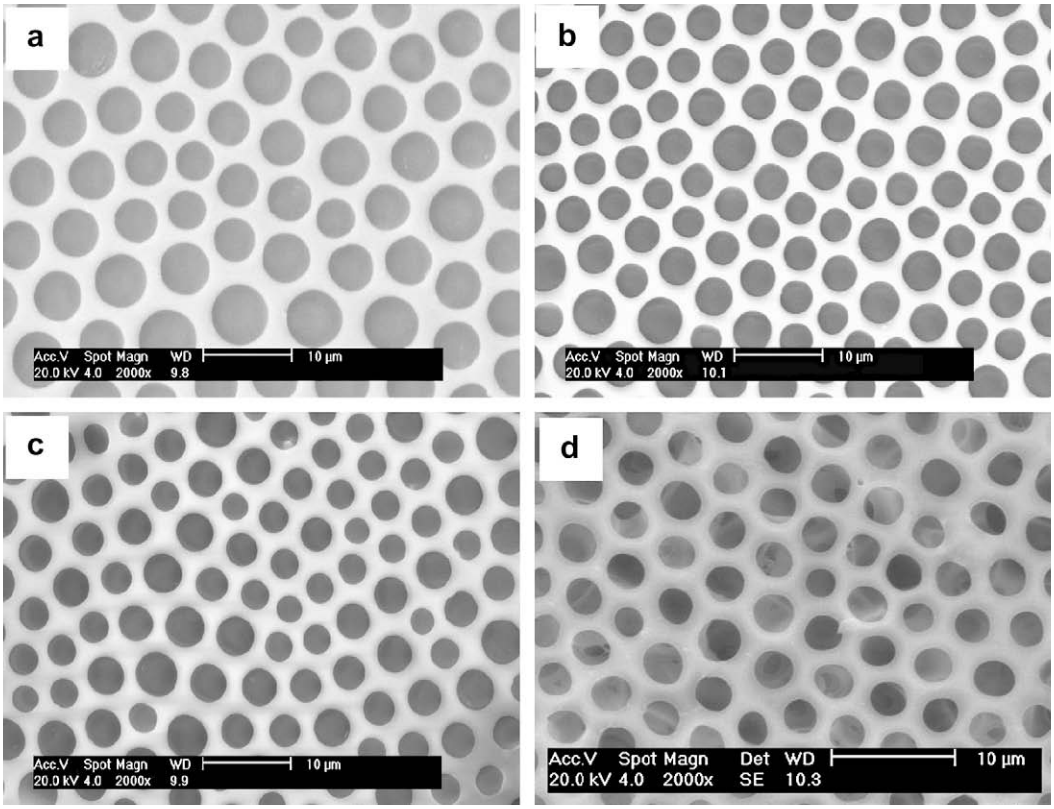

Fig. 1. ESEM surface images of PANI/PC composite films at different polymerization times of aniline: (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h. The honeycomb PC film shown in (a) was prepared by evaporating PC/$CHCl_3$ solution (0.05 g/mL) directly at 75% relative humidity at 25 °C.

coating method. In the present work, however, the PC films with ordered structure were prepared *via* water-assisted method using nano- and micro-sized water droplets as templates, first described by François et al. [15]. In this technique, water vapor condenses into water droplets on the surface of a solution during solvent evaporation; the water droplets are self-organized and closely packed hexagonally by the convectional flow or the capillary force generated at the solution front [16]. After complete solvent and water evaporation, traces of water droplets remain in the polymer film to form honeycomb structure. This method has been widely applied to the preparation of polymers with a highly regular porous array due to its simple process, low cost and dynamic control over the morphology of the resultant pores. Using the honeycomb ordered porous PC film prepared by water-assisted method as templates to prepare PANI composite films has not to date been reported.

This paper concerns the PANI/PC composite film successfully prepared by *in situ* chemical oxidation polymerization of aniline, which was preorganized on the surface of honeycomb ordered porous PC film fabricated by water-assisted method *via* hydrogen bonding. The surface and cross-sectional morphology, electrical and thermal properties of the PANI/PC composite film have been studied.

2. Experimental section

2.1. Materials

Polycarbonate (PC) was purchased from Bayer China Co. Ltd. PC was dissolved in chloroform and precipitated in excess methanol for three times. The number average molecular weight (M_n) and polydispersity index (PDI) were 7.46×10^3 and 2.45, respectively, which were determined by gel permeation chromatography (Waters Co.) with polystyrene standard using tetrahydrofuran as mobile phase. Sodium orthovanadate was purchased from Shanghai Chemical Reagent III Co. Aniline (Tianjin Chemical Reagent III Co.) was purified by *vacuum* distillation before use. The solvent chloroform (Tianjin Chemical Reagent III Co.) was dried by traditional method. Other reagents were purchased from Tianjin Chemical Reagent III Co. as analytical grade and used as received without further purification.

2.2. Fabrication of honeycomb PC films

The typical preparation procedure of the honeycomb PC film was carried out in a glove box with a thermometer and a hydrometer to monitor the atmosphere conditions. A small electric fan was used to keep convection of the atmosphere in the box. The PC was dissolved in dried chloroform with a solution concentration of 0.05 g/mL for 5 h. Then 0.30 mL of polymer solution was directly cast on a clean glass substrate at 25 °C under 75% relative humidity. After complete evaporation of the solvent, the porous film with a diameter of 3 cm was formed.

2.3. Preparation of PANI/PC composite films

Honeycomb ordered PC film prepared as above was immersed in 0.325 mol/L aniline/1 mol/L HCl aqueous solution and was allowed to stand for 24 h. Then an equal volume of oxidant solution containing sodium orthovanadate (0.125 mol/L) in 1 mol/L HCl aqueous solution was added. The reaction was carried out for different times under ice-bath condition, for example, 1 h, 2 h and 3 h. Subsequently the film was washed with distilled water and 1 mol/L HCl.

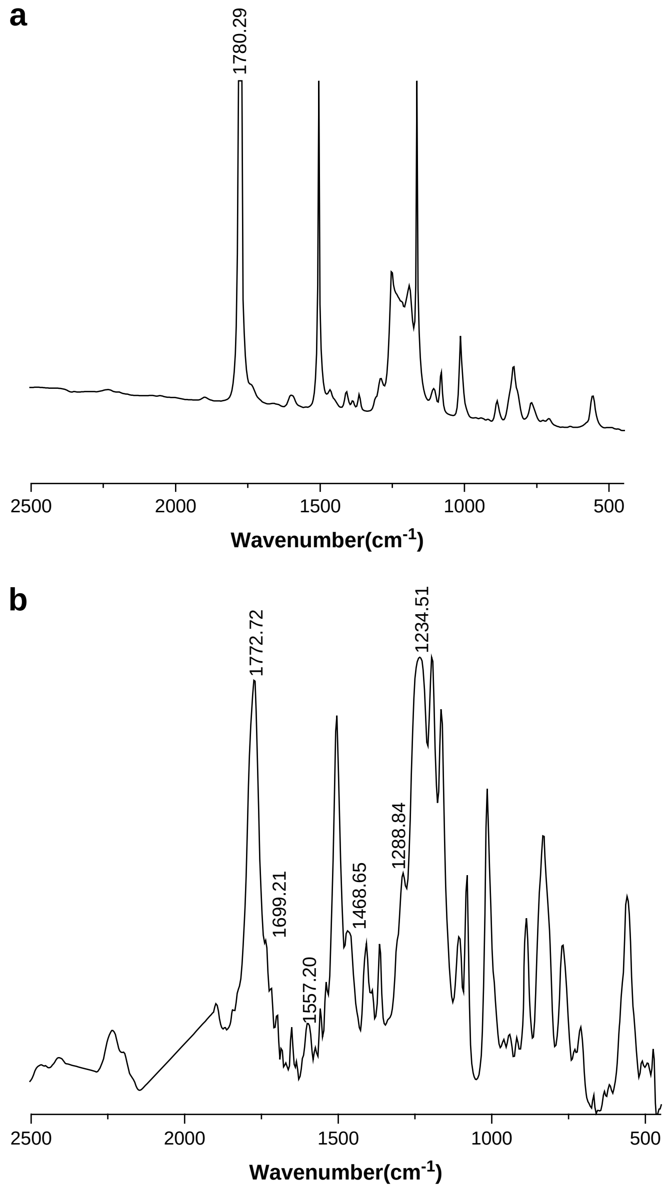

Fig. 2. FT-IR spectra for (a) PC and (b) PANI/PC composite film in the IR (2500–500 cm^{-1}) region.

Finally the PANI/PC composite film was dried in *vacuum* at 50 °C for 24 h.

2.4. Film characterization

The surface and cross-sectional morphology of the film was studied by environmental scanning electron microscopy (ESEM; XL30, Philips Electron Optics, Netherlands) with the operating voltage of 20.0 kV. The cross-section was obtained by fracturing the film at liquid nitrogen temperature. The FT-IR spectrum of the film was carried out using Bio-Rad FTS 6000 (Bio-Rad Inc., America). The thermogravimetric analysis (TGA) thermogram was obtained by using an NETZSCH TG 209 (METZSH Inc., Germany) thermal analyzer from ambient to 800 °C at a scanning rate of 10 °C/min in air atmosphere. Electrical conductivity of the composite film was performed by Hall Effect Measurement System (HL5550PC, Accent Optical Technologies Ltd., UK).

3. Results and discussion

3.1. Preparation of PANI/PC composite film

The preparation of the honeycomb ordered PC film was much similar to our previous reports [12,17–20]. Fig. 1a shows the surface morphology image of ordered porous PC film prepared from PC/$CHCl_3$ solution (0.05 g/mL) under 75% relative humidity at 25 °C. The resultant honeycomb PC film was then immersed in aniline/HCl aqueous solution. When the oxidant solution containing sodium orthovanadate was added, the PANI was gradually formed on the surface of honeycomb porous PC. The color change of film from white to green indicated obviously the formation of the PANI on the honeycomb ordered PC substrate, because the green color was the characteristic of the emeraldine form of PANI (conducting form). The surface morphology images of PANI/PC composite films at different polymerization times of aniline are presented in Fig. 1b–d, respectively, for 1 h, 2 h and 3 h. To determine the formation of PANI on the surface of PC film, the FT-IR spectra of the PC and PANI/PC composite film with polymerization time of 3 h were recorded by using a Bio-Rad FTS 6000 FTIR instrument and are shown in Fig. 2.

From the infrared spectrum of PANI/PC composite film (Fig. 2b), it was obviously found that two peaks at 1288 cm^{-1} and 1234 cm^{-1} corresponding to the C–N stretching region of PANI, and another two peaks at 1557 cm^{-1} and 1468 cm^{-1}, corresponding, respectively, to the stretching region of quinone ring and to the benzene

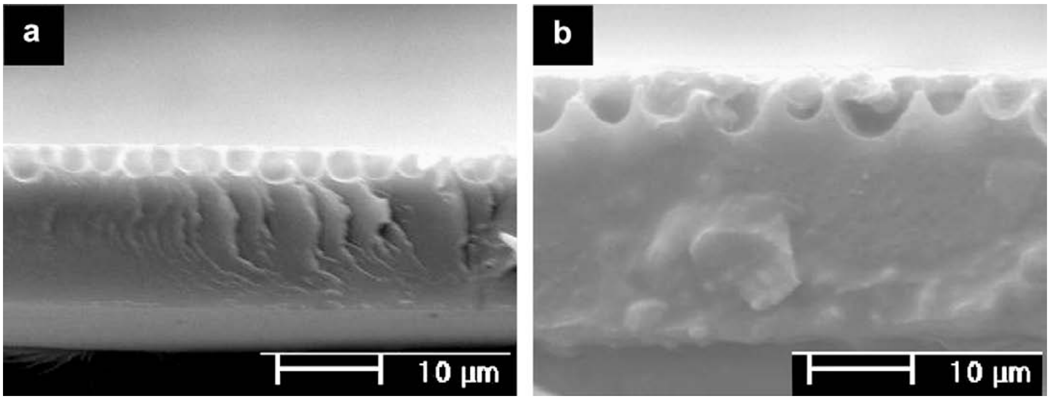

Fig. 3. ESEM cross-section images of (a) PC and (b) PANI/PC composite film, polymerization time of aniline: 2 h. The honeycomb PC film shown in (a) was prepared by evaporating PC/$CHCl_3$ solution (0.05 g/mL) directly at 75% relative humidity at 25 °C.

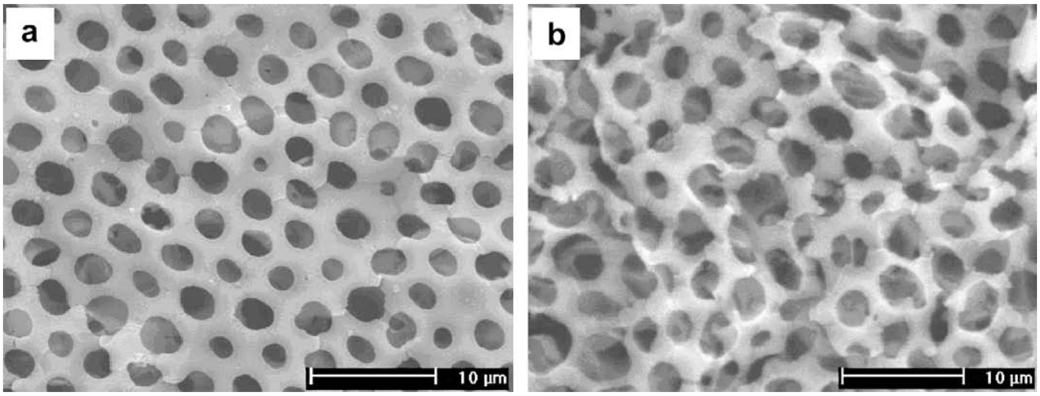

Fig. 4. ESEM surface images of PANI films obtained by immersing the PANI/PC composite films in $CHCl_3$, polymerization time of aniline: (a) 2 h, (b) 3 h.

ring in PANI. This result indicated that a PANI layer had been successfully fabricated on the surface of PC film. On the other hand, the shift of the C═O characteristic stretching region from 1780 cm^{-1} to 1772 cm^{-1} (Fig. 2a and b) and a new peak at 1699 cm^{-1} suggest the interaction of hydrogen bonding between C═O of PC and N–H of PANI. Jeevananda et al. [21] also reported the similar results when they prepared PANI/PC composite materials *via* emulsion polymerization using sodium dodecanesulphonate as surfactant and dopant.

With the increase of polymerization time, the thickness of pore wall increased gradually. The cross-section morphology of PANI/PC composite film was also observed and was partly shown in Fig. 3. From Fig. 3, it was obvious that there was a layer of PANI on the top of PC honeycomb film. The growth mechanism of the PANI on the honeycomb PC film could be explained as follows. Aniline hydrochloride monomer was preorganized onto the surface of PC film *via* the main hydrogen bonding interaction between N–H of the anilinium cation and C═O of the PC. Adsorbed anilinium cation was then polymerized by adding the oxidation reagent. With the polymerization going on, the resultant amount of PANI on the PC film increased gradually. With the increase of polymerization time, however, the changes in the thickness of PANI layer were not obvious enough to determine its exact thickness by comparing the cross-sectional SEM images of PANI/PC composite films with those of PC films, probably due to the PANI layer formed on the surface of PC templates is very thin.

After the removal of the PC substrate by immersing the resultant PANI/PC composite film in chloroform for at least 24 h, the green honeycomb ordered PANI film was obtained and many cracks could be found due to the rigidity and brittleness of PANI film during the transfer (Fig. 4). This result indicated the template role of the honeycomb PC film. Further, the longer of polymerization time, for example 3 h, the crimple and crack on the PANI film were more visible (Fig. 4b). It could be explained as follows: the contraction of PANI may occur due to the density difference between the monomer ($\rho_{aniline} = 1.16$ g/cm^3) and the polymer ($\rho_{PANI} = 1.40$ g/cm^3) during the course of polymerization, which is similar to the work of Trautmann et al. [22]. The *in situ* polymerization kinetics of aniline on the PC film is also in progress. It is interesting to note that the thinner PANI layer was formed on the surface of PC film than that formed on the surface of PSPF from their cross-sectional SEM images, probably because of the weaker hydrogen bonding interaction between the protonated amino groups within the aniline and carbonyl groups within PC leading to the inefficient preorganization of aniline on the PC film substrate.

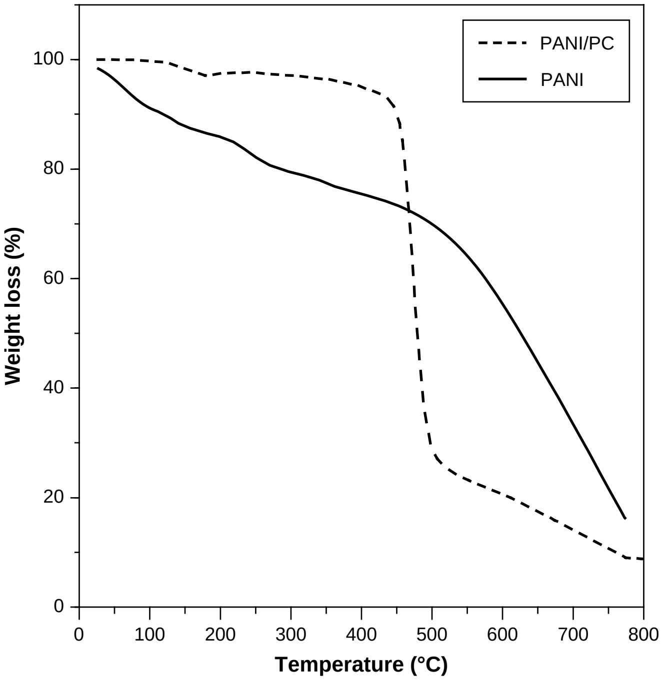

Fig. 5. TGA profiles of PANI/PC composite film with polymerization time of 2 h and PANI, which was prepared by immersing the PANI/PC composite films in $CHCl_3$ and dried in *vacuum* at 50 °C for 24 h.

3.2. Thermostability of the PANI/PC composite film

The thermal stability of PANI/PC composite films was investigated by thermogravimetric analysis (TGA), which was performed with an NETZSCH TG 209 instrument at a heating rate of 10 °C/min in atmospheres of air and the results are depicted in Fig. 5. The data obtained from Fig. 5 are also summarized in Table 1. From Table 1, it can be found PANI film shows a three-step thermal degradation process in the temperature range 50–160, 160–350, and 350–760 °C for moisture loss, dopant loss (HCl), and main-chain degradation of PANI, respectively.

Table 1
Data obtained from TGA plots of PANI film and PANI/PC composite film (see Fig. 5).

Sample code	Degradation temperature range (°C)		
	First step	Second step	Third step
PANI	50–160	160–350	350–760
PANI/PC	110–300	300–500	500–800

Table 2
Relation between polymerization time and electrical conductivity of PANI/PC composite film.

Composite film	Polymerization time (h)	Surface resistivity ($\times 10^4\ \Omega/\square$)	σ (s/cm)	σ^a (s/cm)
1	1.0	38	0.03	0.05
2	2.0	1.41	0.71	1.29
3	3.0	0.72	1.39	3.39

[a] Electrical conductivity data of PANI/SPSF composite films at corresponding polymerization time to that of PANI/PC composite films were cited from the literature [12].

Similarly, PANI/PC composite film also shows three-step weight loss. The first step weight loss occurs in the range 100–400 °C due to moisture and dopant loss; the second step in the range 400–500 °C is due to PANI degradation. The third step is due to PC degradation and is in the range 500–800 °C. The relatively higher thermal stability of the PANI/PC film than that of the PANI film should be attributed to the (i) hydrogen bond formation between –NH of PANI and –C=O of PC and (ii) the thermal stability of PC is very much higher compared to PANI.

3.3. *Electrical conductivity of the PANI/PC composite film*

The electrical conductivity of PANI/PC composite films prepared from various polymerization times was studied by traditional four-probe technique and the results are summarized in Table 2.

At the polymerization time of 1 h, the surface resistivity of the PANI/PC composite film decreased to $38 \times 10^4\ \Omega/\square$, which indicated the formation of the conducting PANI layer on the surface of the PC film, considering high resistivity of PC film itself. With the increase of polymerization time (from 1 h to 2 h), the sharp change of the surface resistivity (from $38 \times 10^4\ \Omega/\square$ to $1.41 \times 10^4\ \Omega/\square$) was observed in accordance with the ESEM results of PANI/PC composite films. As shown in Fig. 3a and b, there was an obvious change in the thickness of the pore wall for PANI/PC composite film compared with the PC honeycomb film. With the polymerization time further increasing, polymerization of aniline adsorbed on the PC film tended to complete and/or the formation of the PANI layer which may prevent the diffusion of the oxidant reagent. Thus, the change of the surface resistivity (from 1.41×10^4 to $0.72 \times 10^4\ \Omega/\square$) was not obvious (for example, polymerization time from 2 h to 3 h).

As can be seen from Table 2, the electrical conductivity of the resultant PANI/PC composite film increased gradually, which was similar to our recent results of PANI/PSPF composite films [12], probably due to the fact that well-compacted PANI layer on the surface of honeycomb ordered PC film was formed with the increasing of polymerization time. However, it can be obviously found that PANI/PC composite films had lower electrical conductivity within the same polymerization time than that of PANI/PSPF composite films. Although the influencing factors on the electrical conductivity of organic semiconductor film materials are very complicated, this result can be tentatively rationalized as follows: the formation of a well-compacted PANI layer is influenced by the interaction mode of aniline with the functional groups on surface of the honeycomb porous substrate. PSPF has a strong electrostatic interaction with aniline producing a more regular preorganized structure on its surface compared with the PC substrate by a weaker hydrogen bonding, leading to more efficient producing of conducting PANI network on the surface of PSPF film. Therefore, the electrical conductivity of PANI/PC composite film increased more slowly than that of PANI/PSPF composite film within the same polymerization time. So, it maybe possible to produce some new conducting composite films with different electrical performances and controllable ordered structure by simply controlling the morphology of substrate film used as templates, the interaction between the polymeric precursors and the substrate as well as the polymerization time to meet the practical request.

4. Conclusions

In this paper, the conductive PANI layer with honeycomb ordered structure was successfully formed by a simple one-step chemical oxidation polymerization of aniline, which was first adsorbed onto the surface of honeycomb ordered PC films used as template *via* hydrogen bonding. The resultant PANI/PC composite film with the ordered porous structure and electrically conductive surface had higher thermal stability than PANI itself. This kind of composite film may have potential applications in conducting film material, sensor materials and scaffold to induce other ordered morphologies.

Acknowledgements

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