

Preparation and Characterization of Polyaniline–Polypyrrole Composite from Polyaniline Dispersions

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ABSTRACT: Polyaniline–polypyrrole (PANI–PPy) composite was prepared by *in situ* polymerization of pyrrole in PANI dispersion using FeCl₃·6H₂O as oxidant and sodium dodecyl benzene sulfonate (SDBS) as surfactant. Different synthesis conditions of PANI dispersion including the relative concentration of aniline and SDBS and the amount of acid (HCl) on the morphology and conductivity of the resulting composites were investigated. Fourier transformation infrared (FTIR) spectra, X-ray photoelec-

tron spectroscopy (XPS), thermal gravimetric analysis (TGA), X-ray diffraction (XRD) patterns, and contact angles of the composites showed there existed certain interaction between PANI (or PANI–SDBS) and PPy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3523–3529, 2007

Key words: PANI–PPy composite; PANI dispersion; SDBS

INTRODUCTION

In recent years, conducting polymers have been extensively researched due to their interesting chemical and physical properties and hence their wide range of applications, including rechargeable batteries, gas sensors, and kinds of electronic devices.^{1–3} Among these conducting polymers, polyaniline (PANI) and polypyrrole (PPy) were considered as two of the most promising materials for potential use because of their relatively high conductivity, easy preparation, and environment stability, etc.⁴ Many researchers have reported their studies on the synthesis of PANI and PPy, which showed different morphology with nano- or microstructure, improving characteristic in conductivity, solubility, thermal stability, and so on.^{5–7} PANI or PPy compounded with different materials including inorganic nanoparticles and polymers have been largely prepared because the resulting composites embodied the merits of the different components, which can widen the application fields than the neat ones.^{8–13} However, there is very little literature on the formation of PANI–PPy composite though they both have excellent performances mentioned earlier. Up to now,

electrochemical copolymerization of pyrrole and aniline or electrochemical deposition of PANI and PPy layers on different substrates has been reported to obtain PANI–PPy composite.^{14–18} On the other hand, PANI dispersion as an effective way for application has been prepared via the aid of kinds of steric stabilizers or surfactants.^{19–23} Various PANI/polymer blends have been prepared using PANI dispersions as media.^{12,24} For example, PANI/polystyrene and PANI/poly(methyl methacrylate) blends were obtained by simple mixing of the aqueous PANI–dodecyl benzene sulfonic acid (DBSA) dispersion with an aqueous emulsion of the polymers.¹² Nevertheless, polymerization of different monomers occurring in PANI dispersions seems to be a blank field in the application of PANI dispersions to the best of our knowledge. We have successfully prepared PANI dispersions using sodium dodecyl benzene sulfonate (SDBS) both as dopant and surfactant with proper acid and aniline concentration and the dispersions showed excellent stability without precipitation for at least 1 year.²⁵ In this article, we tried to prepare PANI–PPy composite from these dispersions and we found there existed certain interaction between PANI and PPy, which could be confirmed by their morphology, conductivity, X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and contact angle measurement. The different preparation conditions and even the storing time of the dispersions would have all significant influence on the properties of the resulting composites.

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MATERIALS AND METHODS

Materials

Aniline was distilled under vacuum before use and other reagents were used as received.

Synthesis of PANI dispersion

A typical experiment was done as follows: SDBS aqueous solution with different concentration was mixed with small amount of HCl solution (0.36M). The acid was used to convert SDBS to its acid form DBSA and provide H⁺ to induce the polymerization of aniline. Aniline was dissolved in the above-mentioned solution under stirring. Ammonium persulfate (Aps) in powder state was then added into the mixture solution and stirred for 1 min. The so-obtained solution was kept unstirred at 25°C for about 2 h until the color turned dark green, which indicated the emeraldine salt had been formed. Different preparation conditions were listed in Table I and the total volume of the solution was 100 mL.

Synthesis of PANI-PPy composite

Every 50 mL of the obtained PANI dispersion storing with half a year was used as reaction medium. No further treatments were carried out to remove the unreacted oxidant and monomer and they were stored in common containers at room temperature before use. 0.33 g of pyrrole was dropped into the dispersion with stirring for 10 min. Then, 50 mL of aqueous solution containing 1.35 g of FeCl₃·6H₂O was added dropwise into the above solution. The mixture was kept stirring for 8 h at room temperature. Finally, the composite was collected by filtration, washed by deionized water and ethanol continuously, and dried in vacuum at room temperature

for 48 h. The concentrations of the pyrrole monomers and oxidants were both 0.05M.

Characterization

Fourier transformation infrared (FTIR) spectra of the samples were measured on an FTIR-8400s (Shimadzu) spectrometer in the transmission mode. Standard KBr technique was applied. Resolution of the measurements was equal to 4 cm⁻¹. As for the PANI in dispersion state, a drop of PANI dispersion was dropped onto a piece of silicon wafer and a green film was then formed on the wafer, which was used for the FTIR measurement.

The morphology of the PANI-PPy composites were directly observed using scanning electron microscopy (SEM, SSX-550, Shimadzu) without gold coating.

The conductivity of powder pellets at room temperature was measured by a typical four-probe method (SDY-5).

XPS was conducted using a VG ESCALAB MK II spectrometer (VG Scientific, UK) employing a monochromatic Mg-K_α X-ray source ($h\nu = 1253.6$ eV). Peak positions were internally referenced to the C1s peak at 284.6 eV.

TGA was performed using a Mettler-Toledo SDTA851^e thermogravimetric analyzer in air atmosphere from room temperature to 700°C at a heating rate of 10°C/min.

XRD pattern was taken with a Shimadzu XRD 6000 instrument at a 5°/min scanning speed from 5 to 60°. Cu K_α ($\lambda = 0.154$ nm) was adopted at room temperature.

The contact angles with water for the sample pellets were measured on a contact angle system (FAT200).

RESULTS AND DISCUSSION

Formation of the composite

The solution color turned from dark green to black when the oxidant was dropped into it, indicating the polymerization of pyrrole and the formation of PANI-PPy composite. On the basis of the following results, we could primarily confirmed that there existed certain interaction between PANI (or PANI-SDBS) and PPy: (1) The pure PANI dispersion left nearly nothing on the filter paper when it was filtered, but the filtrate was transparent when the composite was formed, indicating the colloid PANI had been destroyed during the polymerization of pyrrole and PANI nanoparticles might be compounded with the newly formed PPy, though the increase of ion strength that would result in the precipitation could not be excluded; (2) A black film could be strongly

TABLE I
Preparation Conditions of PANI Dispersions
and the Conductivity of the Corresponding
PANI-PPy Composites

No.	Aniline (M)	Aps (M)	SDBS (M)	HCl (mL)	Conductivity (S cm ⁻¹)
1	0.01	0.01	0.025	1.65	<0.1
2	0.01	0.01	0.025	3.3	0.70
3 ^a	0.01	0.01	0.025	6.6	1.15
4 ^a	0.01	0.01	0.025	10	2.76
5	0.005	0.005	0.025	3.3	0.22
6 ^b	0.02	0.02	0.025	3.3	1.00
7 ^b	0.04	0.04	0.025	3.3	0.23
8	0.01	0.01	0.01	3.3	0.66
9	0.01	0.01	0.05	3.3	1.40
10	0.01	0.01	0.1	3.3	1.46

^a The dispersion has slight precipitation.

^b The dispersion has serious precipitation.

adsorbed on the wall of the vessel when pure PPy was synthesized in aqueous solution; however, in the composite system, the wall was nearly transparent. Therefore, we considered when the pyrrole was added into the PANI dispersion, a certain attraction between pyrrole and PANI (or PANI-SDBS) might be formed due to adsorption or electrostatic interaction. The surfactants, on the other hand, would attract pyrrole around them to locate the monomers though they played an important role to stabilize the PANI particles.

FTIR spectra

FTIR spectra of the PANI and the corresponding PANI-PPy composite (Sample 2 in Table I) are shown in Figure 1. Figure 1(a) gives the spectrum of the PANI and the characteristic peaks at ~ 1562 and 1461 cm^{-1} , which are assigned to C=C stretching of the quinoid and benzenoid rings, respectively, can be clearly observed. From Figure 1(b), the presence of characteristic peaks of both PANI and PPy confirms the formation of PANI-PPy composite in certain degree.^{15,17} For instance, the peaks at 1539 and 1452 cm^{-1} are corresponding to typical pyrrole rings vibration; the peak at 1298 cm^{-1} is due to the presence of aromatic NH groups; the peak at 1165 cm^{-1} presents the C—H in plane bending and the broad band around $800\text{--}900\text{ cm}^{-1}$ should be ascribed to the C—H out-of-plane vibration. Besides, the presence of the peak around 2900 cm^{-1} confirms the formation of the doping of SDBS, because this peak can be attributed to the stretching vibration mode of the methylene in SDBS.²⁶ The other samples from different synthesis conditions showed no apparent difference with Sample 2.

SEM

The SEM images of PANI-PPy composites from different synthesis conditions of PANI dispersions are presented in Figure 2, respectively. As can be seen from Figure 2(a–d) (Samples 1–4 in Table I), the composites obtained from the systems with various acid amounts, the samples showed similar sponge-like structure comprising of short nanofibers. The nanofibers give average length of $300\text{--}500\text{ nm}$ and width of $30\text{--}50\text{ nm}$, respectively, and they compact with each other to give a soft surface from observation with lower magnification. As we know, in the typical synthesis of PPy with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as oxidant, the products always appear as granular particles. However, in the PANI dispersion, pyrrole was first attracted to the micelles constructed by the surfactants. Because PANI nanoparticles have already been stabilized around the micelles, the pyrrole would have interaction with the surfactant and also the

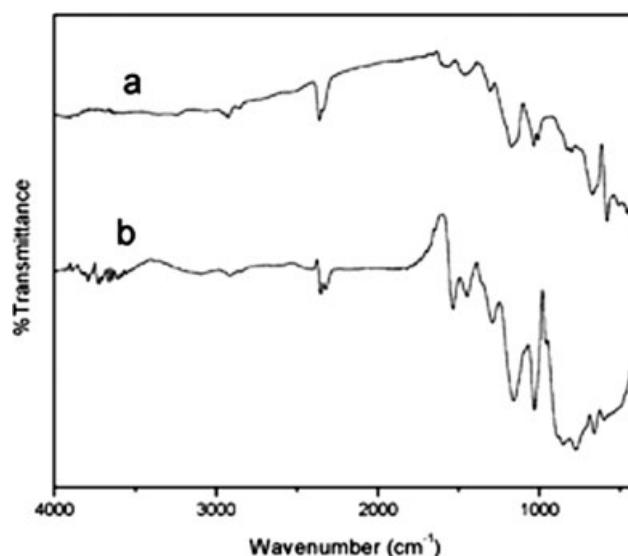


Figure 1 FTIR spectra of PANI (a) and PANI-PPy composite (b, Sample 2 in Table I).

PANI due to adsorption as discussed earlier. When the oxidant was added into the solution, the pyrrole began to polymerize and could be compounded with PANI because of the electrostatic interaction between them. Since the polymerization was carried out around the micelles and PANI has already been stabilized by the micelles, the PPy would be generated along a certain direction. Finally, the nanofibers were formed and compacted due to the interaction between the resulting composites and the surfactants.

Figures 2(e–g) show the SEM images of PANI-PPy composites with different aniline amounts for the preparation of PANI dispersions (Samples 5–7 in Table I). From the images, one can find that when aniline was used with a relative small or big amount, the resulting samples did not give good nanofiber structure. We considered that in a lower aniline concentration, the composite could not be well formed due to the weak interaction between PANI and pyrrole (or PPy), which would not lead to the good oriented polymerization. On the other hand, when aniline was used too much, the PANI dispersion could be destroyed because the surfactants would not have ability to stabilize the PANI particles, and hence the composites would also be difficult to be formed. From Figure 2(g), we can find the granular particles have already existed in the system, which was consistent with the result in common aqueous solution.

The SDBS concentration will also affect the morphology of the resulting composites, which can be observed from Figures 2(h–j) (Samples 8–10 in Table I). A lower SDBS concentration would not lead to the good formation of the sponge-like structure,

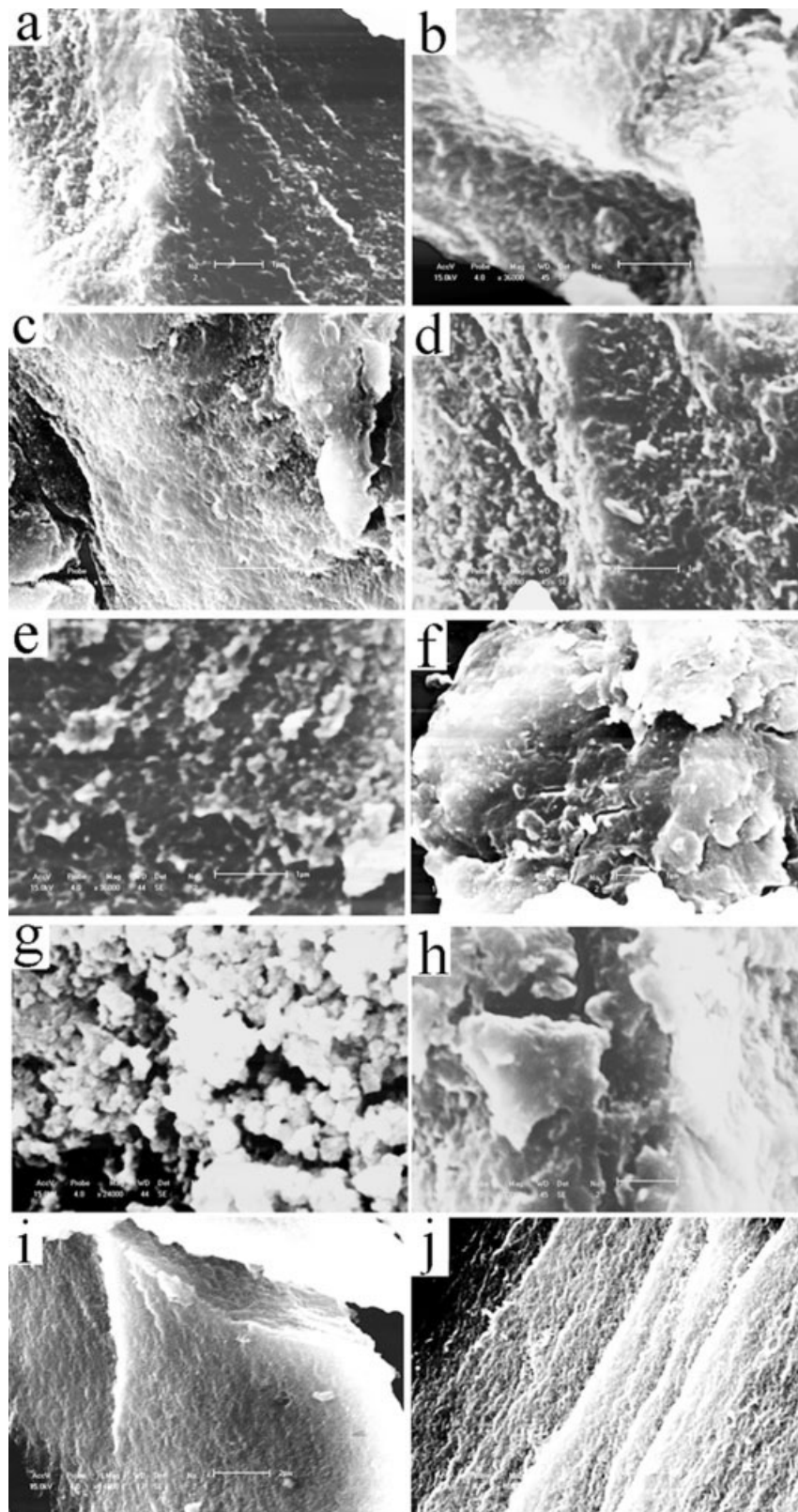


Figure 2 SEM images of PANI-PPy composite from PANI dispersions (a–j represents Sample 1–10 in Table I, respectively).

because the dispersion was not stable under such condition. Conversely, the dispersion became more stable when the concentration of SDBS reached

0.1M, and as a result, the composite obtained from this system showed more uniform nanofiber structure.

Conductivity

Typically, the conductivity of the samples lies on two aspects: microscopic and macroscopic conductivity. The former depends on the doping level, conjugation length, and chain length, etc., whereas the macroscopic conductivity is related to some external factors such as the compactness of the samples.¹⁰

The conductivity of the PANI-PPy composites obtained from different conditions is listed in Table I. On the basis of the results of SEM observation, one can find that Samples 5–8 (Table I) show poor ability to form good composites due to the weak interaction between PPy and PANI (or PANI-SDBS). From the aspect of the acid amount, it is found that the conductivity of the composites increased from less than 0.1 to nearly 3 S cm⁻¹ with the amount of acid from 1.65 to 10 mL, respectively, because the doping level was improved with the increasing of the acidity. On the other hand, when the aniline was in a relatively small or big usage in the dispersions, the resulting composites showed low conductivity with the value of 0.22 S cm⁻¹ (0.005M of aniline) and 0.23 S cm⁻¹ (0.04M of aniline), respectively. We thought this decreasing conductivity might be originated from the unsuccessful complex of PANI and PPy, which could reduce the conjugation or chain length of the composites.

Though the conductivity of the composites obtained from systems with different surfactant concentrations showed little difference, we found a good compactness of the nanofibers would be benefit for the improvement of the conductivity. For example, the composite from 0.1M SDBS solution had a better morphology than that from 0.025M as can be seen from Figure 2, so the conductivity of the former one was twice more than that of the later (1.46–0.70 S cm⁻¹).

Apart from that, we also compared the conductivity of the samples obtained from dispersions storing

with different time, i.e., 1 year, half a year, and 1 day, respectively (the synthesis conditions were the same as that of Sample 9 and the dispersions were stored in liquid state until they were used for the preparation of the composites). We surprisingly found the time-effect of the dispersions on the conductivity of the samples was very strong though the samples did not give significant difference in their morphology. The values of their conductivity were 17.5 (1 year), 1.4 (half a year), and 0.22 S cm⁻¹ (1 day), respectively. Then, we considered a longer storing time would be helpful for a stronger interaction between the surfactant and the PANI, which would improve the combination of the PANI and PPy in the later synthesis process as a result.

XPS

To further investigate the interaction between the different components in the composite, two samples were selected for the next characterization, e.g. Samples 2 and 7. Because they represented the composites with good (Sample 2) and bad complex (Sample 7), which could be indicated from their morphology and conductivity as discussed earlier. Figure 3(a,b) present the XPS (N1s) spectra of Samples 2 and 7, respectively. The N1s core-level spectra can be deconvoluted by assigning binding energy of 398.2, 399.6, and 401.2 eV for imine (—N=), amine (—NH—) and cationic nitrogen atoms (N⁺).^{17,27} We can hardly find the signal of —N= in both the samples, indicating that the imine nitrogen atoms were completely protonated in these samples. Table II lists the binding energies with their corresponding atomic concentrations calculated from their respective peak area. Combining Figure 3 and Table II, we can find the determined degrees of protonation for Samples 2 and 10 are 34.3 and 25.8%, respectively, which was consistent with their conductivity values. We

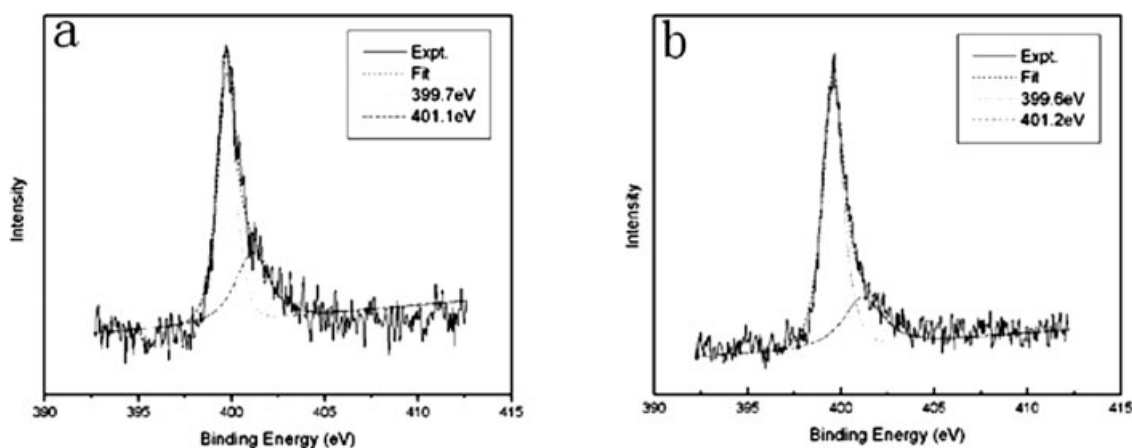


Figure 3 XPS N 1s core level spectra of PANI-PPy composites (a, Sample 2; b, Sample 7 in Table I).

TABLE II
Binding Energies (eV) with Their Corresponding
Atomic Concentrations of Various Charge-Corrected
XPS Components of N 1s Peaks

Peak	Component 1	Component 2	
N 1s	Sample 2	399.7 (65.7)	401.1 (34.3)
	Sample 10	399.6 (74.2)	401.2 (25.8)

contributed the lower degree of protonation of Sample 7 to two reasons: (1) the aniline amount in Sample 7 was much higher than others including Sample 2, which perhaps led to poorer protonation in the unstable dispersion system; (2) the composite was not well formed as its SEM image showed and the worse complex might result in a lower protonation. It should be noted that the distinction between protonated species from PANI or PPy was not feasible.

TGA

The TGA curves of Samples 2 and 7 are presented in Figure 4. The results show that Sample 2 with better complex between PANI (or PANI-SDBS) and PPy had better thermal stability than Sample 7, which can be concluded from the decomposition temperatures of the two samples. The maximum decomposition temperature of Sample 2 was 317°C, whereas that of Sample 7 was 305°C. On the other hand, an extra decomposition step with temperature of ~ 490°C was found in the TGA curve of Sample 2, because in this system, the surfactant SDBS was used as a good dopant counterion and hence improved the stability of the resulting composites.²⁷ Besides, the complete decomposition temperature of Sample 2 (~ 633°C) was higher than that of Sample 7

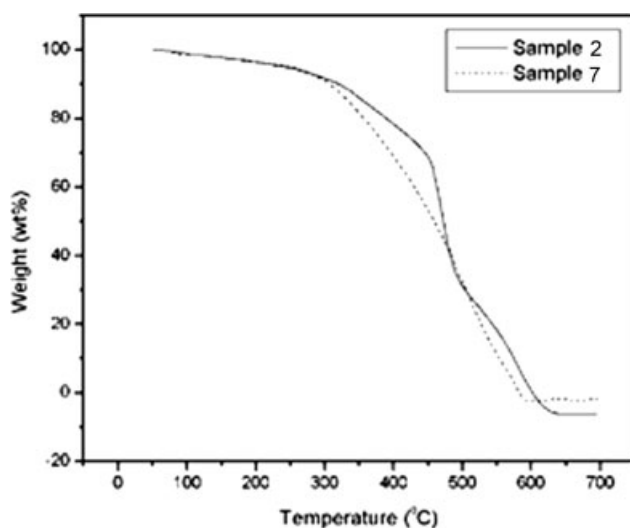


Figure 4 TGA curves of PANI-PPy composites.

(~ 588°C), further indicating the better thermal stability of Sample 2.

XRD

The XRD patterns of Samples 2 and 7 are represented in Figure 5. It shows that Sample 2 was amorphous with only a broad peak around 22°. However, Sample 7 presented isomorphous characteristic with two main peaks centered at ~ 20 and 25°. The XRD pattern of Sample 7 was quite similar to that of PANI synthesized in sodium dodecylsulfate (SDS) aqueous solution, in which aniline was polymerized at the interface of the micelles formed by SDS, and hence a good crystallinity was obtained.²⁸ This allowed us to consider that PANI and PPy were not well compounded in Sample 7 because of the bad dispersion condition, but the PANI had already been doped with SDBS and the isomorphous result might be attributed to the PANI component in Sample 7. Whereas, composite was well formed in Sample 2 and the interaction between the different components perhaps resulted in an amorphous characteristic.

Contact angle

Samples 2 and 7 both exhibited hydrophobic behavior and their contact angles with water were 117.54 and 111.64°, respectively. The higher value for Sample 2 might be due to a stronger interaction between the different components of the composite, which led to a more hydrophobic behavior. The photographs of water on the sample pellets are shown in Figure 6.

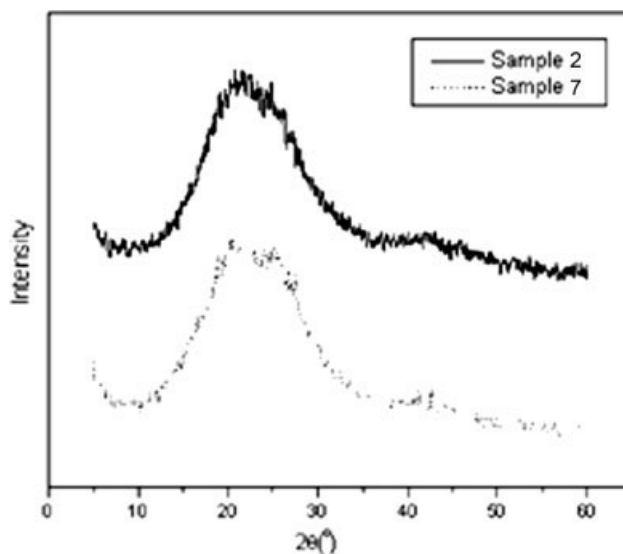


Figure 5 XRD patterns of PANI-PPy composites.

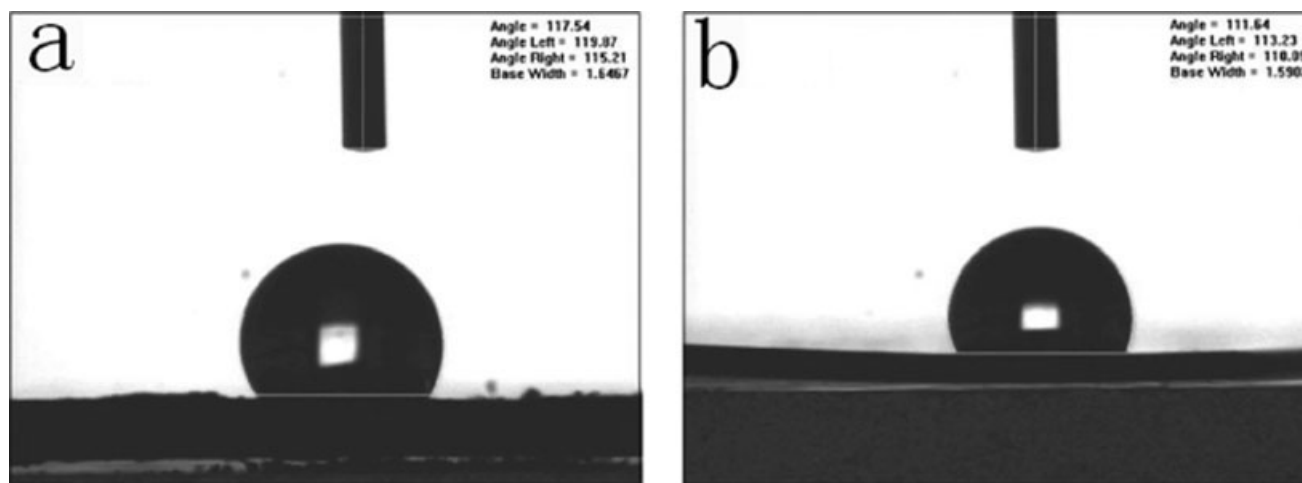


Figure 6 Photographs of water drops on PANI-PPy composite pellets (a-Sample 2; b-Sample 7 in Table I).

Summary

PANI-PPy composite was successfully prepared from PANI dispersion using SDBS as surfactant. It showed that when the PANI dispersions were well formed through appropriately selecting the synthesis conditions, composites with high conductivity and excellent sponge-like morphology comprising of nanofibers could be obtained. Otherwise, the products presented aggregates with granular particle morphology and low conductivity. Comparison between the composites from good and bad dispersions was conducted using different manners including XPS, TGA, XRD, and contact angle measurement, and the results indicated a higher doping level and stronger interaction were formed in the sample obtained from the more stable dispersion. It should be noted that a dispersion storing for longer time would benefit for the formation of PANI-PPy composite with higher conductivity.

References

- MacDiarmid, A. G. *Angew Chem Int Ed* 2001, 40, 2581.
- Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv Mater* 2002, 14, 99.
- Virji, S.; Kaner, R. B.; Weiller, B. H. *Chem Mater* 2005, 17, 1256.
- MacDiarmid, A. G. *Synth Met* 1997, 84, 27.
- Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. *J Am Chem Soc* 2003, 125, 14793.
- Yang, C.-H.; Chih, Y.-K.; Cheng, H.-E.; Chen, C.-H. *Polymer* 2005, 46, 10688.
- Jang, J.; Oh, J. H. *Langmuir* 2004, 20, 8419.
- Flittion, R.; Johal, J.; Maeda, S.; Armes, S. P. *J Colloid Interface Sci* 1995, 173, 135.
- Cochet, M.; Maser, W. K.; Benito, A. M.; Callejas, M. A.; Martínez, M. T.; Benoit, J.-M.; Schreiber, J.; Chauvet, O. *Chem Commun* 2001, 16, 1450.
- Chen, A.; Wang, H.; Zhao, B.; Li, X. *Synth Met* 2003, 139, 411.
- Saunders, B. R.; Saunders, J. M.; Mrkic, J.; Dunlop, E. H. *Phys Chem Chem Phys* 1999, 1, 1563.
- Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, A. *Synth Met* 2000, 110, 189.
- Rodrigues, P. C.; Lisboa-felho, P. N.; Mangrich, A. S.; Akcelrud, L. *Polymer* 2005, 46, 2285.
- Sari, B.; Talu, M. *Synth Met* 1998, 94, 221.
- Akundy, G. S.; Rajagopalan, R.; Iroh, J. O. *J Appl Polym Sci* 2002, 83, 1970.
- Rajagopalan, R.; Iroh, J. O. *Electrochim Acta* 2002, 47, 1847.
- Rajagopalan, R.; Iroh, J. O. *Appl Surf Sci* 2003, 218, 58.
- Cakmak, G.; Küçükyavuz, Z.; Küçükyavuz, S. *Synth Met* 2005, 151, 10.
- Kuramoto, N.; Geniès, E. M. *Synth Met* 1995, 68, 191.
- Stejskal, J.; Špirkova, M.; Riede, A.; Helmstedt, M.; Mokreva, P.; Prokeš, J. *Polymer* 1999, 40, 2487.
- Somani, P. R. *Mater Chem Phys* 2003, 77, 81.
- Stejskal, J.; Sapurina, I. *J Colloid Interface Sci* 2004, 274, 489.
- Moulton, S. E.; Innis, P. C.; Kane-Magulre, L. A. P.; Ngamna, O.; Wallace, G. G. *Curr Appl Phys* 2004, 4, 402.
- Su, S. J.; Kuramoto, N. *Synth Met* 2000, 108, 121.
- Xing, S. X.; Zhao, C.; Jing, S. Y.; Wang, Z. C. *J Mater Sci* 2006, 41, 2761.
- Zhang, X.; Zhang, J.; Song, W.; Liu, Z. *J Phys Chem B* 2006, 110, 1158.
- Wei, X.-L.; Fahlman, M.; Epstein, A. J. *Macromolecules* 1999, 32, 3114.
- Kim, B.-J.; Oh, S.-G.; Han, M.-G.; Im, S.-S. *Synth Met* 2001, 122, 297.