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Electrically conductive polyaniline-sulfonated poly(arylene ether sulfone) composites

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APPLIED PHYSICS LETTERS **87**, 241910 (2005)

Electrically conductive polyaniline-sulfonated poly(arylene ether sulfone) composites

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Electrically conductive composite films from sulfonated poly(arylene ether sulfone) and polyaniline emeraldine base were prepared. The electrical conductivity values, which would be useful for a wide range of applications, were achieved after only 1 min of doping in protonic acid solution. A molecular interaction between the supportive matrix and conductive filler is inferred based on significant difference in the Fourier-transform infrared spectra of the doped and undoped composite films. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2142093]

Electrically conductive and mechanically robust composite materials have found use in advanced technologies including electronics,[1] electro-optical,[2] and energy storage devices.[3] The electrical conductivity of composite films can be tailored to desired application specifications over a wide range by changing the doping level and/or weight fraction of conductive filler. Polyaniline (PANI) is a promising candidate as a conductive filler for polymeric composite films due to its environmental stability, solution processibility, reversible control of electrical properties, and commercial availability. Many researchers have reported supporting PANI using various insulating matrices, such as poly(vinyl alcohol),[4] poly(vinyl chloride),[5] polyacrylonitrile,[6] as well as the commercial ionomer Nafion®.[7] In this study, we introduce a simple chemical route to fabricate electrically conductive films using poly(arylene ether sulfone) copolymers with 35 mol % sulfonation (BPS-35) as supportive matrix and PANI-emerald base (EB) as the electronically conductive polymeric filler. The resulting materials are environmentally and mechanically stable, freestanding films. The synthesis and characterization of poly(arylene ether sulfone) and sulfonated poly(arylene ether sulfone) statistical copolymers and the membrane characteristics for proton exchange membrane fuel cells have been extensively studied by McGrath's *et al.*,[8] where the salt form of poly (arylene ether sulfone) is abbreviated as BPS while the acid form is abbreviated as BPSH.

PANI/BPS-35 composite film is a new promising material from two perspectives. First, the electrical conductivities are high enough for a broad range of applications. Second, the polymer blend method used in this study is superior to chemical and electrochemical synthesis given consideration of time/cost parameters. Freestanding PANI/BPS-35 composite films were prepared using a simple solution casting method. After evaporating the solvent, films were doped in 1 M sulfuric or hydrochloric acid solution for 1 min up to 22 h to convert the PANI-EB into the salt form and to make the films electrically conductive. dc conductivity measurements were performed at room temperature using a Mitsubishi Chemical Laresta-EP MCP-T360 type four point probe. Error resulting from film anisotropy and geometry was minimized by measuring the conductivity at least five different spots on the film. The average of those measurements is presented in this study.

dc conductivity studies of the PANI/BPS-35 composite films indicated a strongly dependency on doping conditions, including dopant type and doping time. The composite films doped with sulfuric acid had one order of magnitude lower resistivity when compared to films doped with hydrochloric acid [Fig. 1(a)]. It is concluded that the counter ion of the dopant has an effective control mechanism of the electrical properties of the composite films. A relatively wide range of doping time was investigated for each dopant. Electrical conductivity appeared after 1 min of doping, indicating relatively fast protonation kinetics.

Regardless of dopant type, 2–3 h of doping time was enough to equilibrate the resistivity of all of the PANI/BPS-35 composite films. Since BPS has hydrophilic regions resulting from disulfonated moieties, which absorb water, the quantity of absorbed water depends on the degree of disulfonation and the acidification method. The percent water uptake of the composite films was calculated using following equation:[9]

$$\text{Water uptake} = \left[\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}\right] \times 100, \qquad (1)$$

where W_{wet} and W_{dry} are the weight of swelled and dry composite films, respectively. The water uptake of BPSH-35 (35 mol % disulfonated copolymer) was 20 wt % when it was acidified with 1 M sulfuric acid at room temperature for 3.5 h. It is believed that BPSH assists the doping process by transporting dopant into the bulk due to its inherent water uptake property.

Figure 1(b) shows the room temperature dc conductivity of the composite films for various PANI loading. The electrical conductivities of a series of composite films having from 10 to 40 wt % PANI were in the range of 2×10^{-7}–2×10^{-3} S/cm for only 1 min of doping with a sulfuric acid solution. After longer doping times (1–4 h), the same composite films achieved higher conductivities (2.3×10^{-6}–0.6 S/cm, respectively). Figure 1(b) also indicates that maximum conductivities reported above changed gradually

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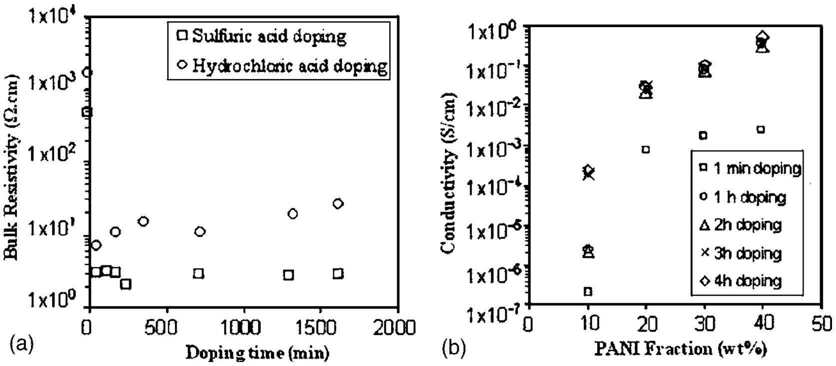

FIG. 1. (a) Bulk resistivity vs doping time plot for 40 wt % PANI containing composite films doped with sulfuric acid or hydrochloric acid. (b) Conductivity vs PANI fraction plot for composite films doped in 1 M sulfuric acid solution at various doping times.

after 15 wt % PANI loading. Hence, the threshold conductivity was reached by 15 wt % PANI loading and 2–3 h doping time. Previous research in our group indicated that the BPS copolymers having significant ionic content coordinates the PANI well up to 20 wt % loading, at which the electrical conductivity percolation threshold has already been reached.[10]

The interaction between PANI and the BPS matrix was investigated via Fourier transform infrared (FTIR) analysis. All films were scrupulously dried to reduced interference(s) from water. Figure 2 shows the FTIR spectra of BPSH-35 copolymer, sulfuric acid doped polyaniline, and both undoped and doped 20 wt % PANI containing composite films. BPSH copolymer has two characteristic peaks at 1030 and 1098 cm^{-1} due to the symmetric and asymmetric stretching of SO_3H groups[11] [Fig. 2(a-I)]. The peaks at 1497 and 1574 cm^{-1} were labeled as benzenoid and quinoid moieties of sulfuric acid doped PANI, respectively. The peak at 1136 cm^{-1} was assigned to aromatic C–H in-plane bending [Fig. 2(a-II) FTIR spectra of doped composite films [Fig. 2(a-IV)] contained the characteristic peaks of BPSH-35 copolymer as well as a peak at 1544 cm^{-1} possibly due to shifting of the PANI peak at 1497 cm^{-1} [see also Fig. 2(b)]. A slight band shift was observed for SO_3 groups [Fig. 2(c)]. These two band shifts could be attributed to the strong interaction—most possibly hydrogen bonding—between SO_3 and NH moieties. However, these interactions described earlier are not observed for the undoped composite film [Fig. 2(a-III)].

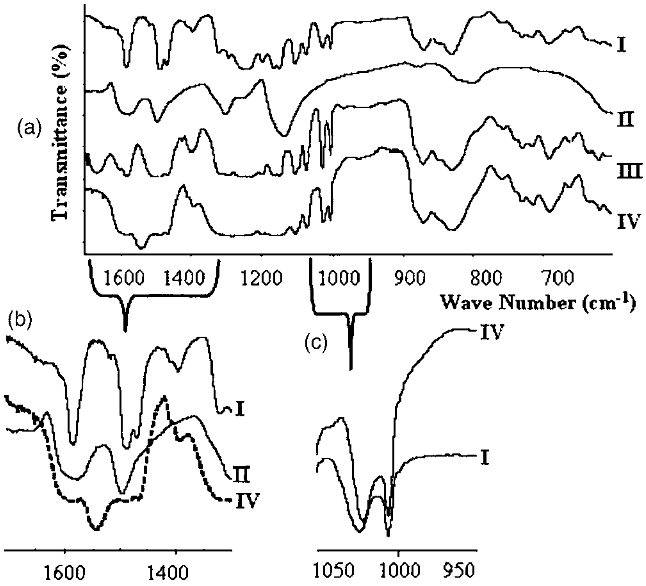

FIG. 2. (a) FTIR spectra of; (a-I) BPSH-35, (a-II), Sulfuric acid doped PANI, (a-III) Undoped PANI/BPS-35 film (20%), (a-IV) Sulfuric acid doped PANI/BPS-35 film (20%); (b) band shift for benzenoid; (c) band shift for SO_3.

Ductile, electrically conductive PANI/BPS-35 composite films with tunable electronic properties were prepared and analyzed. Fourier transform infrared spectroscopies (FTIR) was used for structural confirmation of sulfonated poly(arylene ether sulfone), PANI, and composite films, as well as investigate specific interactions between PANI and sulfonated poly(arylene ether sulfone). The FTIR spectra of the doped and undoped composite films differed greatly, suggesting a molecular interaction between the supportive matrix and conductive filler. Fast doping times (<3 h) was attributed to the hydrophilic nature of the BPS host matrix. These highly conductive composite films are promising candidates for many applications that require a combination of electrical conductivity with mechanical stability.

[1] P. C. Ramamurthy, A. M. Malshe, W. R. Harrell, R. V. Gregory, K. McGuire, and A. M. Rao, Solid-State Electron. **48**, 2019 (2004).
[2] W. E. Howard and O. F. Prache, IBM J. Res. Dev. **45**, 115 (2001).
[3] T. L. Gall, K. H. Reiman, M. C. Grossel, and J. R. Owen, J. Power Sources **119–121**, 316 (2003).
[4] R. Gangopadhyay, A. De, and G. Ghosh, Synth. Met. **123**, 21 (2001).
[5] R. K. Gupta and R. A. Singh, Mater. Chem. Phys. **86**, 279 (2004).
[6] Y. H. Park and C. R. Park, Synth. Met. **118**, 187 (2001).
[7] C. Barthet and M. Guglielmi, J. Electroanal. Chem. **388**, 35 (1995).
[8] S. Wang and J. E. McGrath, *Synthetic Methods in Step-Growth Polymers* (Wiley, New York, 2003), pp. 327–374; Y. S. Kim, F. Wang, M. Hickner, S. Mccartney, Y. T. Hong, T. A. Zawodzinski, and J. E. McGrath, J. Polym. Sci., Part B: Polym. Phys. **41**, 2816 (2003); W. L. Harrison, F. Wang, J. B. Mecham, V. A. Bhanu, M. Hill, Y. S. Kim, and J. E. McGrath, J. Polym. Sci., Part A: Polym. Chem. **41**, 2264 (2003); M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, and J. E. McGrath, Chem. Rev. (Washington, D.C.) **104**, 4587 (2004).
[9] J. B. Mecham, Ph.D. dissertation, Virginia Polytechnic Institute and State University, 2001.
[10] N. Demirci Sankir, J. B. Mecham, R. M. Goff, W. L. Harrison, and R. O. Claus, Smart Mater. Struct. (submitted).
[11] F. Wang, M. Hickner, Q. Ji, W. Harrison, J. B. Mecham, T. A. Zawodzinski, and J. E. McGrath, Macromol. Symp. **175**, 387 (2001).