

# Electrical Conductivity and Electromagnetic Interference Shielding of Polyaniline/Polyacrylate Composite Coatings

Xinli Jing, Yangyong Wang, Baiyu Zhang

Department of Chemical Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, 710049, People's Republic of China

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**ABSTRACT:** Lightweight and flexible composite coatings of *p*-toluene sulfonic acid doped polyaniline (PANI-TSA) with various mass fractions and polyacrylate were prepared for electromagnetic interference (EMI) shielding. Both the volume and surface conductivities of the composite coatings increased with increasing PANI-TSA; furthermore, the volume conductivity showed a typical percolation behavior with a percolation threshold at about 0.21. The EMI shielding effectiveness (SE) of the PANI-TSA/polyacrylate coatings over the range of 14 kHz to 15 GHz increased with increasing PANI-TSA as the direct-current conductivity did.

EMI SE of the coatings at the low frequencies (14 kHz to 1 GHz) was around 30–80 dB, higher than that at the high frequencies (1–15 GHz); this indicated possible commercial application of the coatings for far-field EMI shielding. The highest EMI SE value was 79 dB at 200 MHz with a coating thickness of  $70 \pm 5 \mu\text{m}$ . The moderate SE, light weight, and easy preparation of the coating are advantages for future applications for EMI shielding. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2149–2156, 2005

**Key words:** coatings; conducting polymers

## INTRODUCTION

Electromagnetic interference (EMI), both natural and manmade, is the unwanted energy in the frequency range from below 60 Hz to more than 1000 MHz. EMI shielding is not a new concern but has increased in visibility with the spread of digital electronics, such as the growing use of electronics in aerospace, terrestrial applications, cars, portable consumer devices, and appliances, together with their ongoing miniaturization. Both military and commercial applications are equally concerned about the emissions of electromagnetic radiation from equipment and the susceptibility of equipment to interference; the only differences are the larger shielding frequency range (10 kHz to 40 GHz) and higher shielding effectiveness (SE; no less than 80 dB<sup>1</sup>) required for military use in comparison with commercial applications (300–1000 MHz and no less than 30 dB<sup>1</sup>). In addition, EMI shielding is critical because of health concerns, such as the symptoms of languidness, insomnia, nervousness, and headache on exposure to electromagnetic waves.<sup>2</sup> Information se-

curity is another important concern with EMI shielding, as stated by Van Eck<sup>3</sup> in 1985: information on video display units can be eavesdropped by the picking and decoding of the EMI produced by this type of equipment and displayed on a normal television receiver at a distance of 50 m.

The traditional approach for EMI shielding relies on the use of metallic materials, which supply excellent SE. However, the conventional metallic shields, in the form of bulk sheets, meshes, plating coatings,<sup>4,5</sup> powders (or whiskers), and/or fibers (or filaments) in as-filled polymer composites or coatings, impose severe weight penalties, especially in aerospace applications such as spacecrafts and satellite systems. Although great measures have been undertaken to overcome such weight penalties, such as the coating of ceramic microballoons<sup>6</sup> and carbon fibers<sup>7</sup> with metals for conductive fillers, corrosion, another major drawback of metallic materials, greatly degrades SE of the shields, especially in the joints.<sup>8</sup>

Carbons are also used in EMI shielding applications, mainly as conductive fillers (fibers, particles, powders, filaments, and tubes) in composite materials, because of their electrical conductivity, chemical resistance, and low density. Unfortunately, with the exclusive use of carbon fillers, the conductivity and the resulting EMI shielding performance are not good enough, except for the drawback of the sloughing of carbon fillers, which can otherwise contaminate or damage the electronic devices. The novel class of vapor-grown carbon nanotubes and nanofibers imparts a

Correspondence to: X. Jing (xljing@mail.xjtu.edu.cn).

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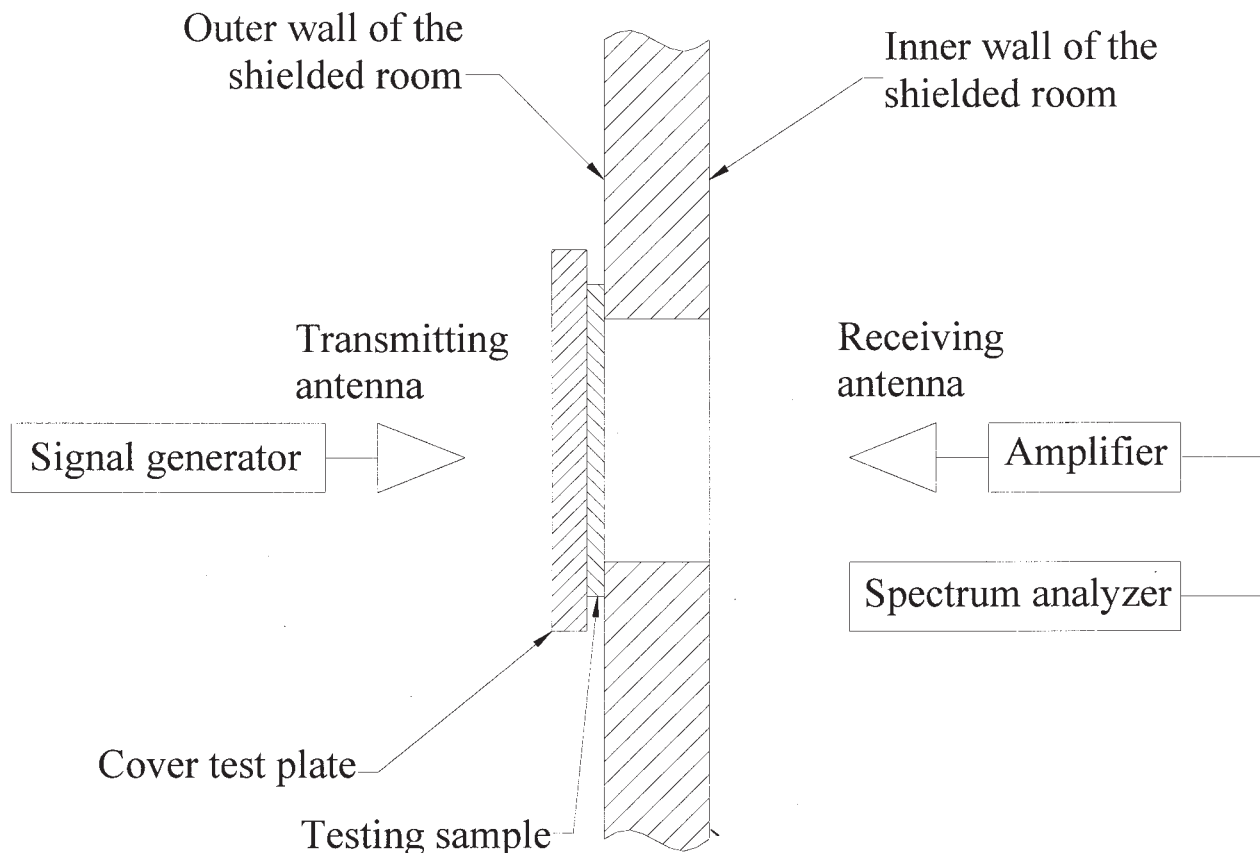


Figure 1 Schematic representation of the test setup.

broad range of conductivity to plastics at far lower loadings than conventional carbon-based additives and simultaneously provides reinforcement and enhanced thermal conductivity. However, the potential of these nanocarbon products is currently limited by their \$50/lb or higher price tags, far higher than the cost of pitch carbon fiber (\$15/lb) and carbon black powder (<\$2/lb).<sup>9</sup>

Intrinsically conducting polymers (ICPs) are attractive alternative materials for EMI shielding because of their light weight, physical flexibility, and tunable shielding response,<sup>10</sup> and many publications have been devoted to the subject.<sup>11–16</sup> Polyaniline (PANI) is one of the most extensively studied ICPs for commercial applications such as corrosion protection<sup>17</sup> and EMI shielding<sup>13,17</sup> because of its environmental stability, higher conductivity, interesting redox properties, and economical efficiency. Although many articles have been published on the EMI shielding of PANI and SE as high as 60 dB has been achieved,<sup>18</sup> the PANI used has been mainly processed through solutions<sup>1,19,20</sup> (one of the major drawbacks of PANI, besides its infusibility) or through melt blending<sup>18,21,22</sup> for processing and applications. It is well known that composites or blends of PANI are preferable because they possess the mechanical properties of the insulating host matrix and the electrical properties of the

conducting PANI guest,<sup>23</sup> and a conducting EMI shielding coating is the most commonly used form in practical applications. In this article, we investigate the conducting and EMI shielding performance of PANI polyacrylate composite coatings. The coatings may find both military and commercial applications because of their high SE, light weight, and ease of preparation.

## EXPERIMENTAL

### Materials

Aniline, ammonium persulfate (APS), methyl isobutyl ketone (MIBK), ethylene glycol mono *n*-butyl ether (EGMBE), *n*-butanol, dimethylformamide (DMF), *p*-toluene sulfonic acid (TSA), and acetone were analytical grade from Xi'an Chemical Reagent Factory (Xi'an, China). Aniline was used after distillation over zinc dust to eliminate the oxidation impurities. Polyacrylate powders with a diameter of 0.125 mm were prepared by ball milling, with the help of a mixed solvent of water and acetone (95/5 v/v), of polyacrylate particles or beads (trademark BR-113, Mitsubishi Rayon Co., Ltd., Tokyo, Japan) with a nominal diameter of 1.0 mm and then were dried and sifted. All other reagents were used as received.

TABLE I  
Equipment Used in the EMI SE Tests

Equipment	Model	Frequency
Spectrum analyzer	HP8566B	20 Hz–26.5 GHz
Signal generator	8850-1	10–100 kHz
Synthetic signal generator	HP8642B	100 kHz–2 GHz
Microwave signal generator	SMP04	2–40 GHz
Amplifier	MH648A	100 kHz–1.2 GHz
Loop antenna	Self-made	20 Hz–30 MHz
Dipole antenna	MP651A	25–1000 MHz
Log periodic antenna	3146	200 MHz–1 GHz
Horn antennas	Self-made	1–18 GHz

### Synthesis

Aniline was chemically polymerized with APS in hydrochloric acid. Freshly distilled aniline (9.31 g, 0.1M) was dissolved in 1 mol/dm<sup>3</sup> hydrochloric acid in a beaker of a certain volume and was brought to the desired temperature (20°C) with magnetic stirring. Afterwards, a hydrochloric acid solution containing 22.8 g of APS (0.1 mol/dm<sup>3</sup>), with the same temperature maintained, was added dropwise to start the polymerization. Within 4 h, the reaction was completed, and the product was collected on a Büchner funnel and washed several times with deionized wa-

ter until the filtrate became colorless. The isolated PANI was further treated with 5.0 wt % ammonia water for 1 h and then washed to neutrality with deionized water. The obtained product was then dried *in vacuo* (50°C) for hours and then powered in an agate mortar/pestle to obtain the emeraldine base (EB) form of PANI powders; the molar ratio of amine nitrogen to imine nitrogen (=N—) was believed to be 1.

EB powders were mixed with an aqueous TSA solution for 20 h and dried afterwards *in vacuo* (50°C) to prepare *p*-toluene sulfonic acid doped polyaniline (PANI-TSA). The TSA used for doping was calculated per the molar ratio of aniline units to TSA:

$$W_{\text{TSA}} = W_{\text{EB}} / (2 \times 91.1) \times R M_{\text{TSA}}$$

where  $W_{\text{EB}}$  and  $W_{\text{TSA}}$  are the weights of EB and TSA, respectively;  $M_{\text{TSA}}$  is the molecular weight of TSA; and  $R$  is the molar ratio of H<sup>+</sup> in TSA to =N— in EB.

### Coating formation

A specific amount of PANI-TSA powders was mixed with 5.0 g of polyacrylate particles and a mixed solvent of MIBK, EGMBE, and *n*-butanol (4/2/1 w/w/w), together with a small quantity of a leveling agent

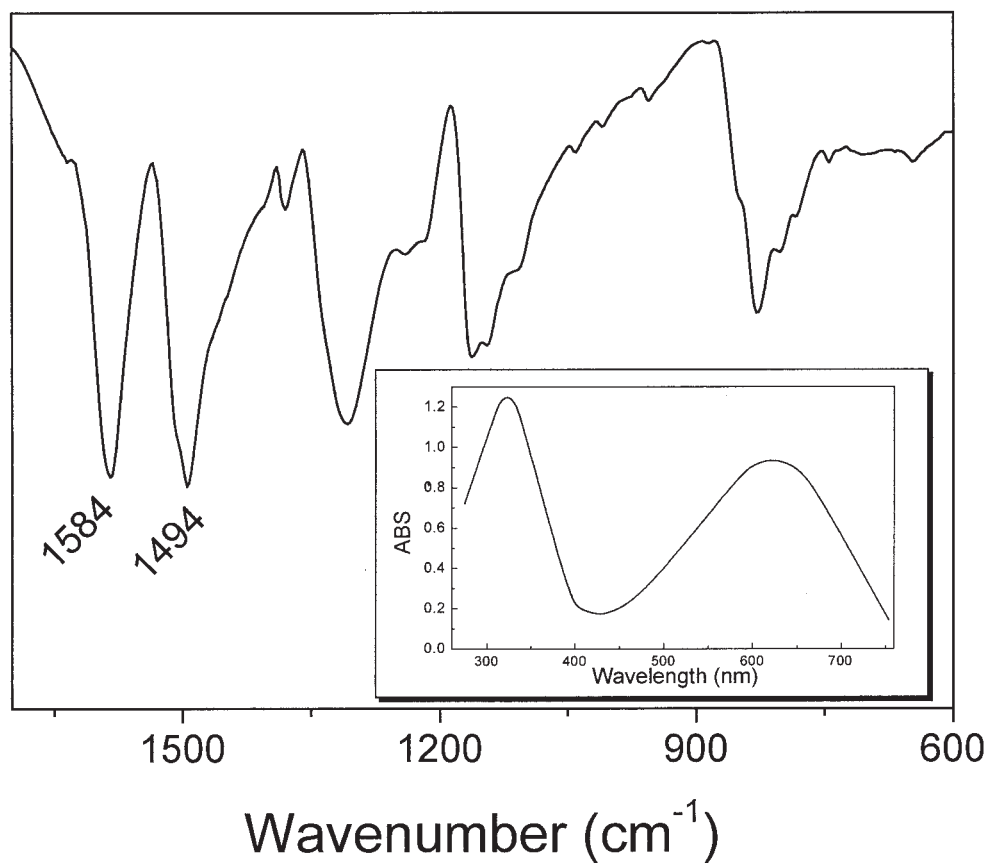


Figure 2 FTIR and UV-vis spectra of EB.

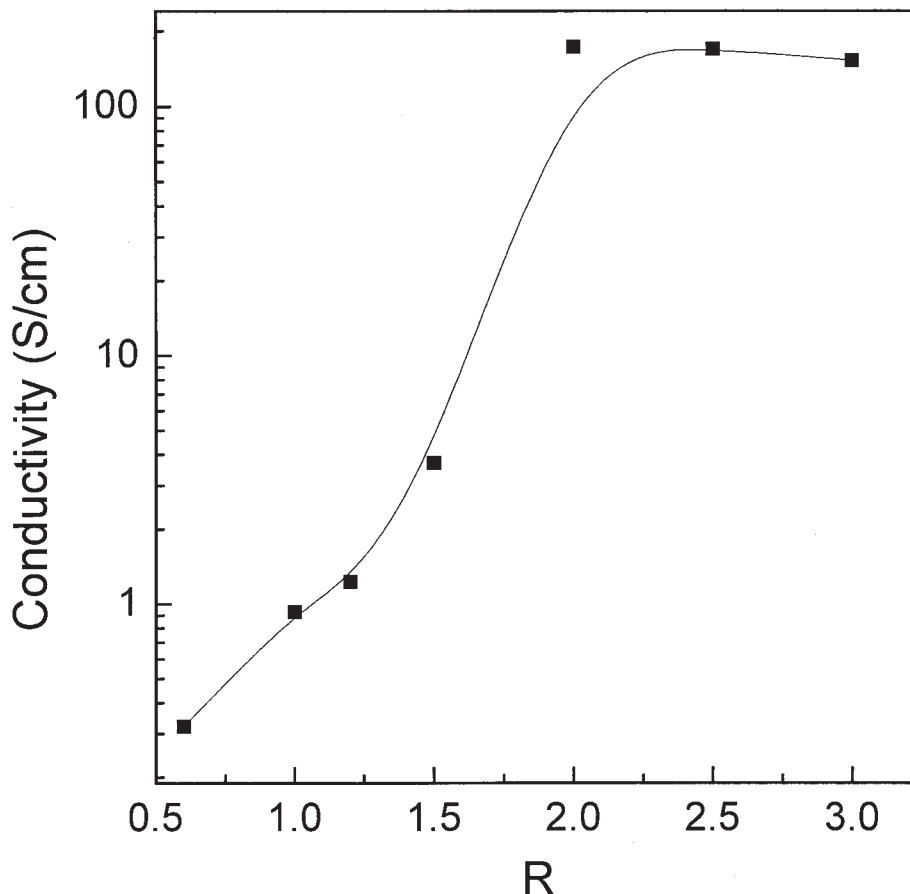


Figure 3 Effect of the amount of the TSA dopant on the conductivities of the PANI-TSA discs.

(Tego Glide 411, Tego Chemie Service GmbH, Essen, Germany) and a dispersant (904S, Deuchem Chemical Co., Ltd., Guangdong, China), and ground in a planetary ball mill (QM-1SP 2L, Nanjing University, Nanjing, China) with stainless steel grinding media for 1.5 h. The obtained paints, with PANI-TSA weight fractions ranging from 25 to 65% in increments of 10%, were sprayed on acrylonitrile-butadiene-styrene (ABS) coupons with dimensions of  $100 \times 100 \times 3.0 \text{ mm}^3$  and copper sheets with dimensions of  $100 \times 100 \times 0.1 \text{ mm}^3$ , which were degreased with ethanol, washed with deionized water, and dried with warm air in advance, for the preparation of the EMI shielding and coating conductivity measuring specimens, respectively. The thickness of the composite coating, denoted PANI-TSA/polyacrylate, was  $70 \pm 5 \mu\text{m}$ , as measured with a micrometer screw gauge.

#### Methods and instrumentation

The ultraviolet-visible (UV-vis) spectrum of EB was recorded between 270 and 800 nm with quartz cuvettes, and pure DMF was used as a reference on a UV-1100 spectrophotometer (Beijing Ruili Analyzing Instrument Factory, Beijing, China); the solution for

subsequent spectroscopic study was prepared by the dissolution of 0.005 g of EB powder in 250 mL of DMF. A Fourier transform infrared (FTIR) spectrum was obtained with an Avatar 360 FTIR spectrophotometer (Thermo Nicolet, Warwick, UK). Solid specimens were prepared by the mixing of their powders with KBr and then were pressed into round pellets. The morphological features of freeze-fractured composite films were detected by a Hitachi S-2700 scanning electron microscope.

The electrical conductivity of the PANI-TSA disk was determined with a four-probe technique on an SZ85 digital multimeter (Suzhou Telecommunication Factory, Tokyo, Japan). The disks were 30 mm in diameter and nominally 1.5 mm thick and were pressed at room temperature for 2.0 min.

The volume conductivity ( $\sigma_v$ ) and surface conductivity ( $\sigma_s$ ) of the coatings were measured according to the method specified by China Aerial Industrial Standards QJ2220.1-92 and QJ2220.2-92 with a CS2676C-1 insulative conductivity tester (Nanjing Changsheng Electronic Factory, Nanjing, China) and an insulative testing electrode box (Shanghai Jingke Co., Shanghai, China). A constant current was passed through the electrodes, and the output voltage was measured

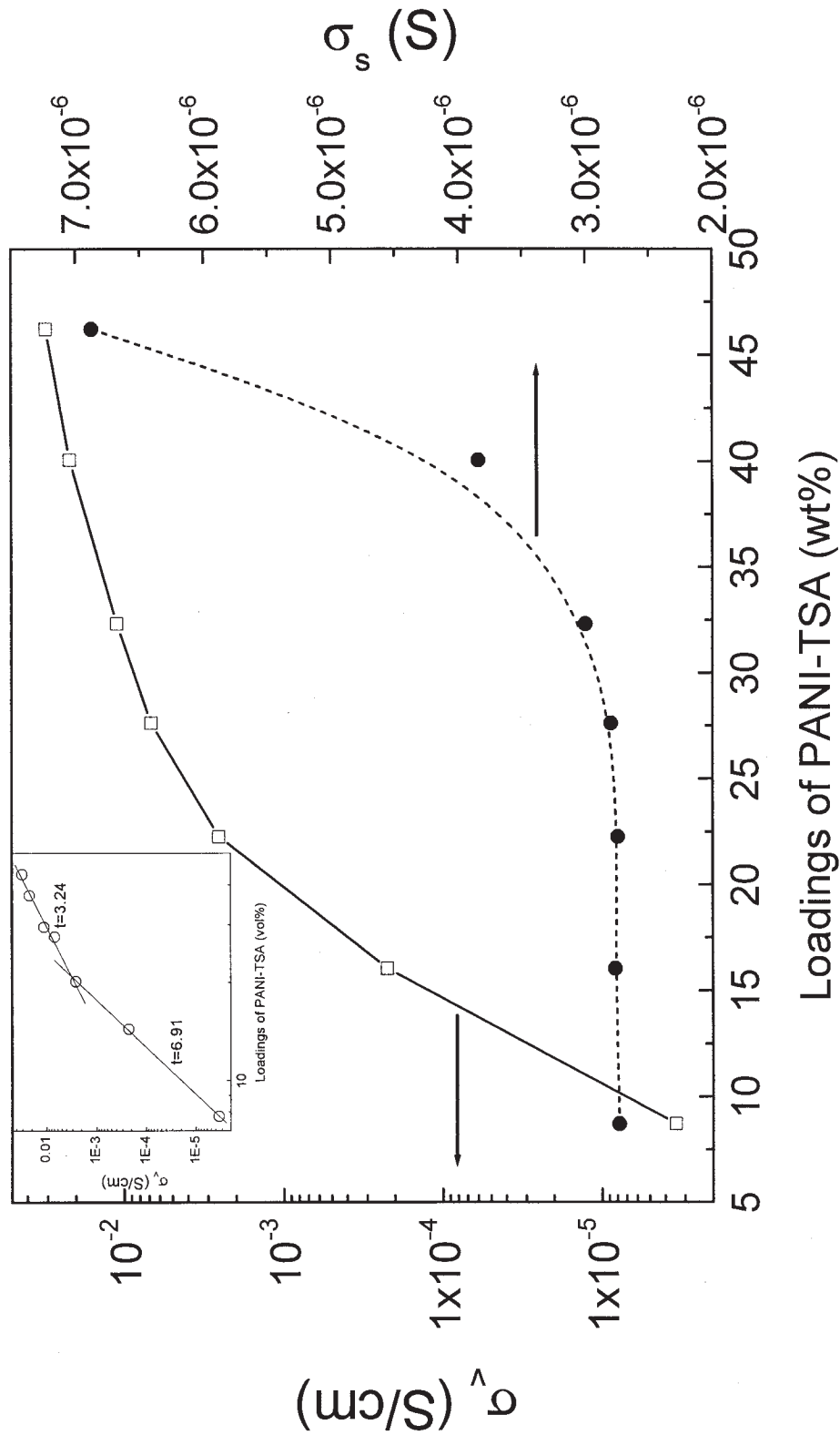
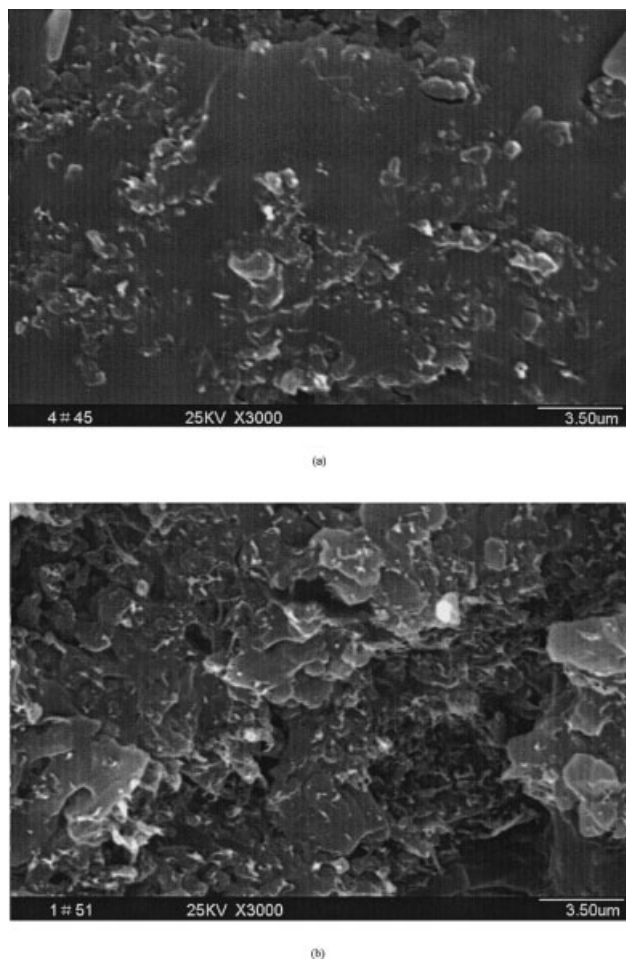


Figure 4  $\sigma_v$  and  $\sigma_s$  of the composite films versus the PANI-TSA loadings.



**Figure 5** SEM photographs of the composite coatings with PANI-TSA loadings of (a) 25 and (b) 35 wt %.

across the corresponding electrodes. The conductivities of the coatings were then determined on the basis of Ohm's law.

EMI SE was measured per the method specified by China National Standard GB12190-90 and American Military Standard MIL-STD-285,<sup>24</sup> as shown schematically in Figure 1, in the EMI test chamber of Xi'an Institute of Electronic Engineering (Xi'an, China). All equipment used to perform the test was well calibrated and is listed in Table I. The receiving antennas and the spectrum analyzers were placed inside the shielded room, and the transmitting antennas, signal generators, and amplifiers were outside the shielded room. The distance between the transmitting and receiving antennas was in accordance with the standards. The test was performed in the frequency range of 9 kHz to 15 GHz with relevant transmitting antennas (Table I). The open reference was taken in free space outside the shielded enclosure. EMI SE was determined by the subtraction of the power level recorded with the testing samples in place from the power level recorded during the open reference mea-

surement: SE (dB) = Open reference - Testing measurement.

## RESULTS AND DISCUSSION

### Spectroscopy of PANI

The UV-vis spectrum of a freshly prepared solution is shown in the inset of Figure 2, which is characterized by two major absorption bands. The first absorption band with a maximum at about 320 nm is associated with the  $\pi$ - $\pi^*$  transition of the conjugated ring systems. The second band at about 630 nm is assigned to a benzenoid-to-quinoid excitonic transition. The peaks at 1584 and 1494  $\text{cm}^{-1}$  in the FTIR spectrum of the polymer (Fig. 2) correspond to the quinonoid and benzenoid structures, respectively. The similar intensities of the two peaks indicate that the polymer is in its intermediate oxidation state. The higher intensity of the benzenoid-related band, in comparison with that of the quinonoid-related band, in the UV-vis spectrum is due to the influence of the existence of the solvent DMF, as we reported recently.<sup>25</sup>

### Conductivities of PANI-TSA discs

The conductivity of PANI is influenced by several factors, such as the molecular weight, the crystallinity of the polymer, and the doping level and type of dopant. TSA is a commonly used dopant for preparing conducting PANI. The doping level of PANI-TSA increased with an increasing amount of TSA used for doping, as can be seen in Figure 3. No high conductivity was achieved when the value of  $R$ , that is, the molar ratio of  $\text{H}^+$  in TSA to  $=\text{N}=-$  in EB as defined before, was small. For example, conductivities of 1.2 and 3.7 S/cm were achieved with  $R$  values of 1.0 and 1.5, respectively. When  $R$  was larger than 2, the conductivities reached the order of magnitude of  $10^2$  S/cm, with the maximum conductivity of 172.5 S/cm obtained with an  $R$  value of 2. However, with a further increase in  $R$  from 2.5 to 3.0, a small decrease in the conductivity was observed, which was probably due to the overburdened TSA that functioned as impurities for conducting PANI-TSA. To achieve higher conductivity in the composite films and to avoid the possible negative effects brought by too much TSA in the films, which would not only function as impurities for conducting PANI-TSA but also degrade the properties, such as the mechanical properties and stabilities of the films, PANI-TSA with an  $R$  value of 2.0 was used as a filler in the following preparation of PANI-TSA/polyacrylate coatings.

### Conductivities of the PANI composite coatings

Both  $\sigma_v$  and  $\sigma_s$  of the composite films increased with the loadings of the conductive filler of PANI-TSA (Fig.

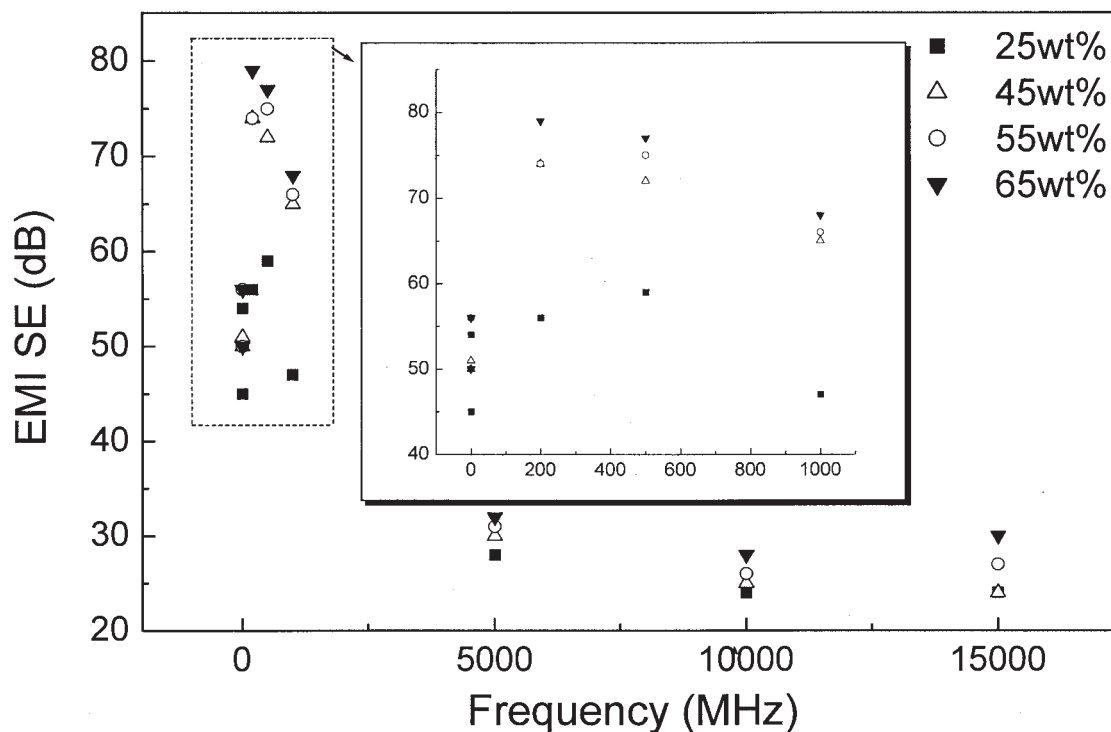


Figure 6 EMI SE of the composite coatings.

4).  $\sigma_v$  as high as 0.030 and 0.021 S/cm was achieved with PANI-TSA loadings of 40.0 and 46.2 wt %, respectively. Based on the densities of 1.36 g/cm<sup>3</sup> for PANI-TSA<sup>26</sup> and 1.20 g/cm<sup>3</sup> for the polyacrylate, the conductivity of the composite coatings versus the volume fraction of PANI-TSA is shown in the inset of Figure 4 on a logarithmic scale. It is clear that  $\sigma_v$  of the composite follows the scaling law of percolation theory:  $\sigma_v = \sigma_0(\phi - \phi_c)^t$ , where  $\sigma_0$  is the conductivity of the conductive fillers,  $t$  is the critical exponent, and  $\phi$  and  $\phi_c$  are the volume fraction and critical volume fraction of the fillers, respectively.<sup>27,28</sup> The exponent  $t$  changed from 6.91 to 3.24 at the critical loading of 20.81 vol % (corresponding to the mass fraction of 24.46 wt %), and this indicated a percolation threshold at about 0.21. The reason for the larger  $\phi_c$  values for the composites, in comparison with the reported value of 0.16 for a three-dimensional system,<sup>27,28</sup> lies in the larger particle size of PANI-TSA [as revealed by scanning electron microscopy (SEM) images in Fig. 5], as demonstrated by many authors.<sup>29–31</sup> In the case of  $\sigma_s$ , all values were in the same order of magnitude of 10<sup>-6</sup> S with PANI-TSA loadings increasing from 8.72 to 46.2 wt %; this was due to the fact that a concentration of the matrix polyacrylate resulted on the surface of the coating with the evaporation of the solvents, and thus a low  $\sigma_s$  value of the same magnitude resulted, regardless of, to some extent, the changing PANI-TSA loadings.

#### EMI SE measurements of the PANI composite coating

The SE values measured from 14 kHz to 15 GHz are given in Figure 6. With a PANI composite coating 70 ± 5 μm thick, SE values of 30–80 dB can be achieved, especially over the low range from 14 kHz to 1 GHz, satisfying the requirement of 30 dB for common commercial applications. Over the whole testing frequency range, SE of the coatings increased with the PANI-TSA loadings, as did the conductivities of the coatings. The increase in SE with increasing PANI-TSA loadings over the low-frequency range of 14 kHz to 1 GHz was more rapid than that over the high-frequency range of 1–15 GHz. For example, when PANI-TSA increased from 25 to 65 wt %, EMI SE at 200 MHz increased from 56 to 79 dB more rapidly than that from 19 to 28 dB at 10 GHz. The more effective shielding performance against the low-frequency electromagnetic waves indicated the dominant shielding characteristics of absorption brought from ICPs.<sup>10</sup> This is different from metal-based materials in which the reflection dominates the shielding characteristics. Although the SE values over the high-frequency range were not satisfying, a further increase in the SE values could be realized, on the one hand, by the multilayer structures of the coating, as suggested by Joo and Lee<sup>19</sup> and Lee et al.,<sup>32</sup> and, on the other hand, by the incorporation of metals<sup>33</sup> or complexation of metal ions<sup>34</sup> with ICPs. No effect of the coating thickness on

the EMI SE was evaluated in this study, but according to Joo and Epstein,<sup>35</sup> SE increased linearly with the thickness except for a thickness below 10  $\mu\text{m}$  for a given PANI sample. Further works concerning the enhancement of EMI SE and the maintenance of SE over time for the PANI composite materials are in progress in our laboratory now.

### CONCLUSIONS

PANI with a conductivity of 172.46 S/cm was obtained via doping with TSA at a molar ratio of TSA to  $=\text{N}-$  of 2. Both  $\sigma_v$  and  $\sigma_s$  of the composites increased with increasing PANI-TSA, and  $\sigma_v$  showed typical percolation behavior with a percolation threshold at about 0.21. EMI SE of the PANI-TSA/polyacrylate coatings over the range of 14 kHz to 15 GHz increased with increasing PANI-TSA, as did direct-current conductivity. EMI SE of the coatings at low frequencies (14 kHz to 1 GHz) was in the order of 30–80 dB, higher than that at a high-frequency range (1–15 GHz). This indicates the possible commercial use of the coatings for far-field EMI shielding applications, in addition to the light weight of the coatings. The highest EMI SE value was 79 dB at 200 MHz with a coating thickness of  $70 \pm 5 \mu\text{m}$ .

### References

- Lee, C. Y.; Song, H. G.; Jang, K. S.; Oh, E. J.; Epstein, A. J.; Joo, J. *Synth Met* 1999, 102, 1346.
- Jang, J. O.; Park, J. W. U.S. Pat. 6,355,707 (2002).
- Van Eck, W. *Comput Security* 1985, 4, 269.
- Mandich, N. V. *Plat Surf Finish* 1994, 81, 60.
- Stefecka, M.; Kando, M.; Matsuo, H.; Nakashima, Y.; Koyanagi, M.; Kamiya, T.; Cernak, M. *J Mater Sci* 2004, 39, 2215.
- Radford, D. W.; Cheng, B. C. *SAMPE Q* 1993, 24, 54.
- Huang, C. Y.; Mo, W. W.; Roan, M. L. *Surf Coat Technol* 2004, 184, 163.
- Carlson, E. J. *Mater Performance* 1990, 29, 76.
- Leaversuch, R. *Plast Technol* 2002, 48, 48.
- Jing, X.; Wang, Y. *Polym Adv Technol* 2005, 16, 344.
- Macdiarmid, A. G.; Epstein, A. J. *Mater Res Soc Symp Proc Electr Opt Magn Prop Org Solid State Mater* 1994, 328, 133.
- Trivedi, D. C.; Dhawan, S. K. *Synth Met* 1993, 59, 267.
- Desai, K.; Sung, C. *Mater Res Soc Symp Proc* 2002, 736, 121.
- Kim, M. S.; Kim, H. K.; Byun, S. W.; Jeong, S. H.; Hong, Y. K.; Joo, J. S.; Song, K. T.; Kim, J. K.; Lee, C. J.; Lee, J. Y. *Synth Met* 2002, 126, 233.
- Paligova, M.; Vilcakova, J.; Saha, P.; Kresalek, V.; Quadrat, O.; Stejskal, J. *Annu Tech Conf Proc* 2003, 2, 2074.
- Koul, S.; Chandra, R. *Annu Tech Conf Proc* 2004, 3, 3039.
- Wessling, B. *Synth Met* 1998, 93, 143.
- Koul, S.; Chandra, R.; Dhawan, S. K. *Polym* 2000, 41, 9305.
- Joo, J.; Lee, C. Y. *J Appl Phys* 2000, 88, 513.
- Joo, J.; Lee, C. Y.; Song, H. G.; Kim, J. W.; Jang, K. S.; Oh, E. J.; Epstein, A. J. *Mol Cryst Liq Cryst Sci Technol Sect A* 1998, 316, 367.
- Colaneri, N. F.; Shacklette, L. W. *IEEE Trans Instrum Meas* 1992, 41, 291.
- Shacklette, L. W.; Colaneri, N. F.; Kulkarni, V. G.; Wessling, B. J. *Vinyl Technol* 1992, 14, 118.
- Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Prog Polym Sci* 1998, 23, 993.
- U.S. Department of Defense, MIL-STD-285, Attenuation Measurements for Enclosures, Electromagnetic Shielding for Electronic Purposes, Method of; Washington, D.C., 1997.
- Wang, Y.; Jing, X. *Polym Test* 2005, 24, 153.
- Stejskal, J.; Gilbert, R. G. *Pure Appl Chem* 2002, 74, 857.
- Sahimi, M. *Applications of Percolation Theory*; Taylor & Francis: London, 1994.
- Zallen, R. *The Physics of Amorphous Solids*; Wiley-Interscience: New York, 1998.
- Wessling, B. *Synth Met* 1991, 45, 119.
- Jing, X.; Zhao, W.; Lan, L. *J Mater Sci Lett* 2000, 19, 377.
- Maaroufi, A.; Haboubi, K.; El Amarti, A.; Carmona, F. *J Mater Sci* 2004, 39, 265.
- Lee, C. Y.; Kim, H. M.; Park, J. W.; Gal, Y. S.; Jin, J. I.; Joo, J. *Synth Met* 2001, 117, 109.
- Lee, C. Y.; Lee, D. E.; Joo, J.; Kim, M. S.; Lee, J. Y.; Jeong, S. H.; Byun, S. W. *Synth Met* 2001, 119, 429.
- Kathirgamanathan, P. *Adv Mater* 1993, 5, 281.
- Joo, J.; Epstein, A. J. *Appl Phys Lett* 1994, 65, 2278.