

# Studies on the Electromagnetic Interference Shielding Effectiveness of Metallized PVAc-AgNO<sub>3</sub>/PET Conductive Films

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Received 7 August 2001; accepted 7 April 2003

**ABSTRACT:** A metal chelate polymer (MCP) of PVAc-AgNO<sub>3</sub> was prepared by adding AgNO<sub>3</sub> salts into the PVAc matrix and was coated on to PET substrate to form PVAc-AgNO<sub>3</sub>/PET films. These films were then treated with NaBH<sub>4</sub> aqueous solution to become the reduced metallized conductive films (RMCF) of PVAc-AgNO<sub>3</sub>/PET. The electromagnetic interference shielding effectiveness (EMI/SE) and the characteristics of these films were investigated. The SE value was measured by the far-field transmission line method. The surface resistivity (Rs) of RMCF with a AgNO<sub>3</sub> content of 15 wt % was found to be below 5 Ω/sq, and the SE value exceeded 20 dB over the frequency range 50–900

MHz. The Rs of RMCF with a AgNO<sub>3</sub> content of 30 wt % was less than 1 Ω/sq, and the SE value even reached 33 dB at 550–650 MHz. It was confirmed by X-ray and scanning electronmicroscope (SEM) analysis that the conducting network, as formed by closely deposited silver atoms on the reduced coating surface, was the dominant pathway for effective electron propagation that contributed to the excellent conductivity of these RMCF (PVAc-AgNO<sub>3</sub>/PET). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 270–273, 2004

**Key words:** conducting polymers; X-ray; surfaces; composites

## INTRODUCTION

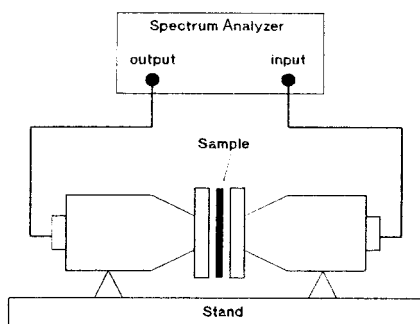
Electromagnetic interference (EMI), such as radio noise, electronic noise, radio-frequency interference, etc., can be regarded as a kind of invisible electronic pollution. It is evident that the electromagnetic fields produced by EMI may cause abnormal operation of computers, electronic devices and instruments, potentially leading to fatal accidents. In order to eliminate the harmful effects of EMI, one practice is to enclose the electronic device completely within a container made of an electrically conducting material so that the electromagnetic wave is absorbed or reflected before being transmitted through it. Metal cases are thus traditionally used to provide EMI prevention for electronic devices. However, with the substantial progress in preparation and processing methods, and the need for effective EMI prevention demanded by the electronic industries, highly conductive polymers have become important materials used to substitute metal cases.<sup>1,2</sup>

The electrical conductivity of polymers can be enhanced by blending conductive fillers, such as metal particles, metal flakes and carbon particles, into the

substrate to form composite conductive polymers<sup>3–6</sup> or by synthesizing intrinsically conductive polymers with conjugated double bond structures.<sup>7,8</sup> However, the composites have weakened mechanical strength due to the non-uniform distribution of fillers, and the intrinsically conductive polymers bear a high cost of preparation and have unstable conductivity.

Another novel approach to increase the conductivity of a polymer is the formation of metal chelates within the polymer.<sup>9–12</sup> In these serial studies, PAI, polyamide,<sup>10</sup> PAAM,<sup>11</sup> PVAc,<sup>12</sup> etc., were identified as having characteristic functional groups that can coordinate with metal salts, such as AgNO<sub>3</sub>, CuCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub> etc., to form the metal chelate polymer (MCP). The MCP can be cast into thin films and treated with reducing agent to become a reduced metallized conductive film (RMCF). By choosing suitable reduction conditions, the surface resistance (Rs) of these RMCF can be made less than 10<sup>0</sup> Ω/sq. The conductivity of these RMCF was found to be stable and excellent, and has potential applications in EMI prevention. However, none of the published articles has discussed in detail the electromagnetic interference shielding efficiency (EMI/SE) of these RMCF. In response to the rising demand for effective EMI prevention polymers, the EMI/SE of the RMCF of PVAc-AgNO<sub>3</sub>/PET prepared from a typical MCP of polyvinyl acetate (PVAc) was investigated.

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**Figure 1** Configuration for electromagnetic shielding effectiveness measurement set-up.

Polyvinyl acetate (PVAc) has strong adhesive properties and was thus used as the matrix polymer in this study. A MCP of PVAc-AgNO<sub>3</sub> was prepared by adding AgNO<sub>3</sub> salts into the PVAc matrix. The resulting MCP was coated on polyethylene terephthalate (PET) plates to form the PVAc-AgNO<sub>3</sub>/PET films. The PET acted as an electrically insulating substrate without EMI shielding capacity and was used to provide tensile support for the MCP coating of PVAc-AgNO<sub>3</sub>. The PVAc-AgNO<sub>3</sub> coating exhibited good adhesion to the PET substrates. The EMI/SE values of the RMCF (PVAc-AgNO<sub>3</sub>/PET) were measured by using the coaxial transmission line test method, and the surface morphology of these films was investigated with X-ray diffraction and scanning electron microscopy.

## EXPERIMENTAL

### Preparation and Characterization of RMCF of PVAc-AgNO<sub>3</sub>/PET

In this study, the MCP of PVAc-AgNO<sub>3</sub> was prepared by introducing AgNO<sub>3</sub> solution into a 20 wt % PVAc formic acid solution according to predetermined weight ratios (wt %) of AgNO<sub>3</sub> to PVAc. This mixture was stirred at room temperature for 24 h. The resulting viscous MCP solution was coated on the clean substrates of PET plates and dried by an electrical oven with forced air circulation at 80°C for 25 min. The formed PVAc-AgNO<sub>3</sub>/PET chelate films were reduced by 500 mL of 1 wt % sodium borohydride solution (NaBH<sub>4</sub>) at 50°C for a suitable time period<sup>12</sup> to become the RMCF (PVAc-AgNO<sub>3</sub>/PET). These films were then washed with distilled water, dried with an air blower, and stored in a desiccator filled with N<sub>2</sub> gas.

### Measurement for EMI Shielding Effectiveness

The EMI/SE of the conductive RMCF (PVAc-AgNO<sub>3</sub>/PET) was measured using the coaxial transmission line test method specified by ASTM D4935-1, as shown in Figure 1. The CoAX88 shielding effective-

ness measurement unit is designed to determine the EMI/SE of planner shielding substances under free space (far-field) conditions.<sup>13</sup> A HM5012 spectrum analyzer was connected to the CoAX88 unit and the software SW5012 was used to calibrate the system. The EMI/SE was measured in the frequency range from 150 KHz to 1 GHz, in which the measurement limit for this spectrum analyzer was 50 dB.

The shielding effectiveness (SE) is given by eq. (1):

$$SE = 10 \log(P_{in}/P_{out}) = 20 \log(E_{in}/E_{out}) = 20 \log(H_{in}/H_{out}) \quad (1)$$

where  $P$  is the energy field,  $E$  is the electrical field, and  $H$  is the magnetic field strength.<sup>14</sup>

In this set-up, the SE was obtained by comparing the signals with and without shielding. The RMCF of PVAc-AgNO<sub>3</sub>/PET being tested were cut into circular specimens of diameter 133 mm. Each specimen was measured three times to obtain the average SE value.

## RESULTS AND DISCUSSION

The common frequency range of EMI extends from 10 Hz to 100 GHz. Electronic devices, such as computer components, are susceptible to an EMI frequency range from 450 KHz to 1 GHz and are more sensitive to RFI of frequency from 500 KHz to 10 MHz.

Table I shows that the conductivity of the RMCF of PVAc-AgNO<sub>3</sub>/PET increases with AgNO<sub>3</sub> concentration (wt %). The  $R_s$  of the RMCF prepared from a 3 wt % AgNO<sub>3</sub> solution was  $1 \times 10^3 \Omega/\text{sq}$ , and that from a 30 wt % AgNO<sub>3</sub> solution was lowered to  $1 \Omega/\text{sq}$ .

Figure 2 indicates the SE of the RMCF of PVAc-AgNO<sub>3</sub>/PET increases as  $R_s$  decreases and the EMI shielding capacity of these RMCF is proportional to the conductivity of the films. All tested RMCF had similar shielding effectiveness to EMI frequency from 50 to 900 MHz, and the relationship between the  $R_s$  and SE value satisfied eq. (2):

$$SE = 20 \log(1 + Z_0/2R_s) \quad (2)$$

**TABLE I**  
Effects of AgNO<sub>3</sub> Concentration (wt %)<sup>a</sup> on  $R_s$  of PVAc-AgNO<sub>3</sub>/PET Films

AgNO <sub>3</sub> <sup>a</sup> (wt %)	$R_s$ ( $\Omega/\text{sq}$ ) (Before NaBH <sub>4</sub> Treatment)	$R_s$ ( $\Omega/\text{sq}$ ) (After NaBH <sub>4</sub> Treatment) <sup>b</sup>
3	$6.25 \times 10^8$	$1.01 \times 10^3$
5	$1.50 \times 10^7$	$5.02 \times 10^2$
10	$3.50 \times 10^6$	$1.00 \times 10^2$
15	$1.00 \times 10^4$	$5.00 \times 10^0$
20	$1.50 \times 10^3$	$1.00 \times 10^0$
30	$1.00 \times 10^3$	$1.00 \times 10^0$

<sup>a</sup> Based on PVAc weight.

<sup>b</sup> By concentration of 1 wt % NaBH<sub>4</sub> solution at 50°C

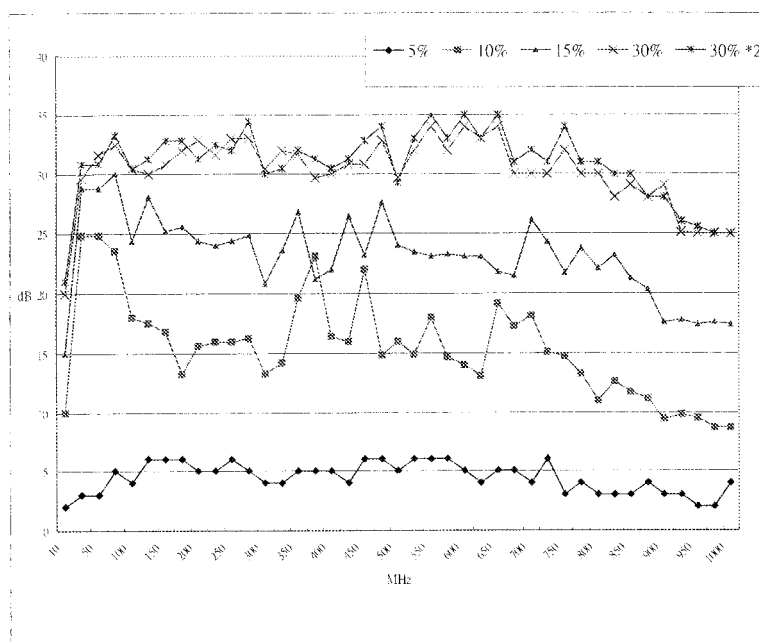


Figure 2 Shielding effectiveness (SE) of the RMCF of PVAc-AgNO<sub>3</sub>/PET.

where  $Z_0$  is the impedance ( $377 \Omega$ ) of free space. Figure 2 also indicates that the  $R_s$  of the RMCF with 15 wt % AgNO<sub>3</sub> is below  $5 \Omega/\text{sq}$ , and the SE value exceeds 20 dB over the frequency range 50 to 900 MHz. For the RMCF prepared from 30 wt % AgNO<sub>3</sub>, the  $R_s$  is less than  $1 \Omega/\text{sq}$ , and the SE value is higher than 30 dB and reaches 33 dB at the frequency range 550 to 650 MHz. Figure 2 also shows that the SE of double layered RMCF (30 wt % AgNO<sub>3</sub>) is not significantly different from that of single layered RMCF (30 wt % AgNO<sub>3</sub>); therefore increasing the concentration of AgNO<sub>3</sub> is a more effective means of increasing the SE value of these RMCF than using a double layered arrangement of RMCF. The results of X-ray analysis are summarized in Table II. From Table II, it can be seen that the X-ray pattern of the RMCF of PVAc-AgNO<sub>3</sub>/PET was identical to that of pure silver atoms, showing that Ag crystallites did exist on the surface of RMCF. Since the SE value of double layered

RMCF (PVAc-AgNO<sub>3</sub>/PET) was nearly the same as that of the single layered, it can be concluded that reflection, rather than absorption, is the dominant factor contributing the EMI attenuation.

The scanning electron microscope (SEM) photograph in Figure 3 depicts the loosely connected "islands" scattered on the surface of unreduced PVAc-AgNO<sub>3</sub>/PET (30 wt % AgNO<sub>3</sub>). The surface appearance of the sample after reduction with NaBH<sub>4</sub> is shown in Figure 4(a) to have a dramatic change on its surface. It is easy to see that the silver metal was generated and agglomerated to form an excellent conductive network on the reduced surface of the RMCF. Because electrons can transfer along the network effectively, the  $R_s$  is diminished to  $10^0 \Omega/\text{sq}$ .

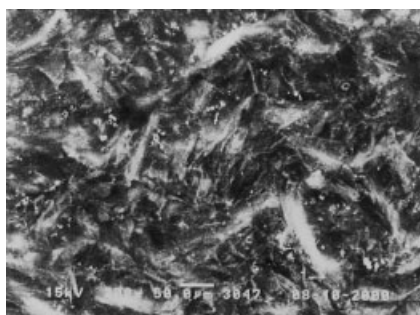
Figure 4(b) shows the cross-sectional area of the RMCF in Figure 4(a). It can be seen more clearly that

TABLE II  
Diffraction Angles ( $2\theta$ ) and Plane Distances ( $d$ )  
Corresponding to Peaks Observed in X-ray Analysis for  
RMCF of PVAc-AgNO<sub>3</sub>/PET (30 wt % AgNO<sub>3</sub>)

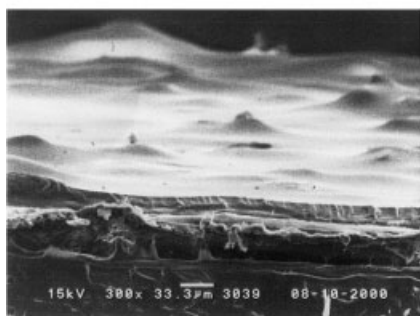
Peaks	Reduced Surface of RMCF (PVAc-AgNO <sub>3</sub> /PET)		Pure Ag Reference (Standard)	
	$2\theta$	$d$	$2\theta$	$d$
1	38.0	2.359	38.12	2.359
2	44.12	2.051	44.27	2.043
3	64.58	1.442	64.42	1.445
4	77.54	1.230	77.47	1.230



Figure 3 Scanning electron microscope<sup>a</sup> photograph showing the surface morphology of unreduced PVAc-AgNO<sub>3</sub>/PET (AgNO<sub>3</sub> 30 wt%) a: A TOPCON SM-300 scanning electron microscope (SEM) was used to inspect the coating surface.



(a)



(b)

**Figure 4** Scanning electron microscope photographs showing the surface morphology of the RMCF of PVAc-AgNO<sub>3</sub>/PET (AgNO<sub>3</sub>30 wt%) (a) After NaBH<sub>4</sub> treatment (b) After NaBH<sub>4</sub> treatment (cross-section)

a thin layer of silver atoms is deposited on the reduced surface of the RMCF (PVAc-AgNO<sub>3</sub>/PET). The silver atoms are densely distributed and closely packed on the surface of the reduced film, leading the reduced film to possess a higher conductivity than the unreduced one. It is obvious that the electron conducting pathway, as provided by this uniform agglomeration of silver atoms, is more effective than the charge transfer mechanism by which the electrons need to migrate along the Ag<sup>+</sup> ions coordinated to the chelate of the polymers, and the firm adhesion of silver atoms on the surface enables the reduced film to achieve a stable conductivity.

## CONCLUSIONS

The RMCF of PVAc-AgNO<sub>3</sub>/PET resemble metal materials in having effective reflection and attenuation to electromagnetic waves higher conductivity, and greater EMI shielding effectiveness. When the surface resistivity of the RMCF was lowered to 1 Ω/sq, the SE value was increased to more than 30 dB over the frequency range 50 to 900 MHz and even reached 33 dB at the frequency range 550 to 650 MHz. With these distinctive SE testing results and the finding that using a single layer is as effective as using a double layer in attenuating the emission of electromagnetic radiation, the RMCF of PVAc-AgNO<sub>3</sub>/PET can be suggested as a potential EMI shielding material, especially for electronic packaging.

The authors are indebted the Hsiuping Institute of Technology for financial support of this work. They are also grateful to Professor Ming-Shing Lin at Da-Yeh University for helpful advice.

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