

Electrical Properties and EMI Shielding Characteristics of Polypyrrole–Nylon 6 Composite Fabrics

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ABSTRACT: Polypyrrole (PPy) was polymerized both chemically and electrochemically in sequence on nylon 6 woven fabrics, giving rise to polypyrrole–nylon 6 composite fabrics (PPy–N) with a high electric conductivity. The stability of the composite prepared by electrochemical polymerization (ECP) on chemical oxidative polymerization (COP) fabric was better than that of the composite prepared solely by the COP process, since the AQSA dopant was able to strongly interact with the PPy main chain and had a large molecular structure. The temperature dependence of the conductivity of the composites was verified over four heating and cooling cycles. The change in conductivity over

these four repeated heating and cooling cycles was affected by the interaction between the thermal stability of the dopant and the rearrangement of the PPy main chain. The electromagnetic interference shielding efficiency (EMI SE) values were in the range 5–40 dB and depended on the conductivity and the layer array sequence of the conductive fabric. The composites with a high conductivity represented reflection-dominant EMI shielding characteristics, which are typical of the EMI shielding characteristics of metals. However, composites with low conductivity showed absorption-dominant EMI shielding characteristics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1969–1974, 2003

INTRODUCTION

With the increasing use of electronic products and telecommunication equipment, electromagnetic interference (EMI) has become a major problem, as it reduces the lifetime and the efficiency of the instruments. To reduce the impact of EMI, EMI shielding materials have been widely investigated. Typically, metals have been used for EMI shielding materials, as they have a high conductivity and dielectric constants. However, metals have disadvantages, such as their weight, corrosion properties, and poor processibility.¹ Electrically conductive polymers can be used as EMI shielding materials to circumvent the disadvantages seen in metals.^{2,3}

Polypyrrole (PPy) is an especially promising conductive polymer for commercial applications, owing to its high conductivity, good environmental stability, and ease of synthesis. However, PPy is insoluble and infusible, which restricts its fabrication, and it has poor mechanical properties.⁴ One of the ways to avoid

these problems is to prepare an electrically conductive textile composite, since these have the resiliency of a textile and excellent mechanical strength and flexibility, but also retain the electrical properties of the conductive polymer.^{5–8}

To prepare conductive composite fabrics, many researchers have focused on chemical oxidative polymerization (COP). As reported by Li et al., a PPy–carbon textile composite was prepared by coating PPy onto carbon fibers.⁵ In addition to this conductive substrate, a conductive composite fabric was prepared using the COP of pyrrole in the presence of a nonconductive matrix, such as nylon 6 fabric,^{6–8} nonwoven fabric,⁹ and acryl fabric.¹⁰ Also, using the microwave-absorbance characteristics of conductive polymers, Contex[®], which is chemically synthesized on PET fabric, was used as camouflage netting by the Milliken Co.¹¹ However, its application to EMI shielding is limited, since the conductive composite fabric from the COP process has a low level of conductivity. There have been some reports on the preparation of conductive composite fabrics using electrochemical polymerization (ECP), which is a generally known method for forming conductive films.^{12,13} The ECP technique has several advantages: It is a simple and inexpensive process and provides ease in controlling the film thickness by an electrical current or potential.¹⁴

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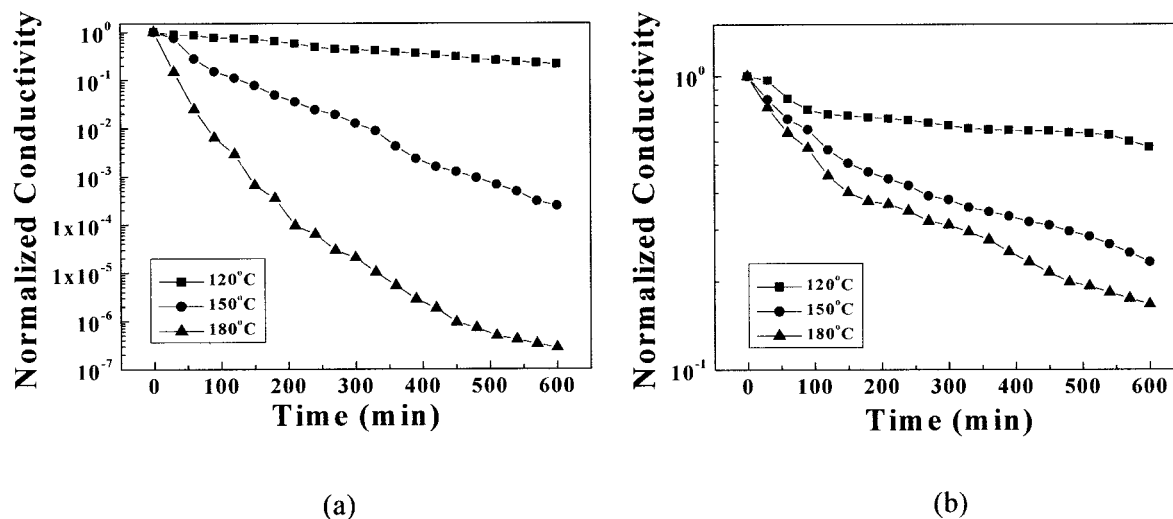


Figure 1 Stability of electrical conductivity of the composite fabrics at elevated temperatures in air: (a) PPy-N prepared by COP; (b) PPy-N prepared by ECP on COP.

Our research focused on a new way to prepare a PPy-fabric composite with a high electrical conductivity and a high EMI shielding efficiency (EMI SE). We investigated the thermal stability and the temperature dependence of the conductivity, EMI SE, and EMI shielding characteristics of the composite fabrics that we fabricated.

EXPERIMENTAL

Materials

Nylon 6 woven fabric (70×70 d, 43×30 cm, Fabric Inspection & Testing Institute, South Korea) was washed with distilled water and dried prior to use, and the pyrrole used (Aldrich Co.) was purified by vacuum distillation. Special reagent-grade ferric chloride (FeCl_3 , Kanto Chemical Co.), benzenesulfonic acid (BSA, Acros Chemical Co.), and the sodium salt of anthraquinone-2-sulfonic acid (AQSA-Na, Aldrich Co.) were used without any further purification.

Preparation of conductive composite fabrics

Conductive polypyrrole-nylon 6 composite fabrics (PPy-N) were prepared using the ECP and COP processes. Details of the preparative procedures can be found in an earlier publication.¹⁵

Evaluation

The electrical conductivity of the composites was measured using the four-probe method.⁷ The thermal stability and temperature dependence of the composite conductivities were measured using a Keithley 2000 multimeter and a Mettler hot stage. A Philips XL 30 field emission scanning electron microscope (FE-SEM)

was used for structural observation of the sample. The frequency dependence of the EMI shielding efficiency of the composites was measured using a Hewlett-Packard 8719 ES vector network analyzer and an S (scattering)-parameter test set in the frequency range 50 MHz to 13.5 GHz.

RESULTS AND DISCUSSION

Thermal stability of electrical conductivity

The conductivity of the composite fabric prepared by COP and that prepared by ECP on the COP fabric was approximately 0.87 and 9.8 S/cm, respectively.¹⁵ The conductivity stability with the temperature of the composite fabrics is shown in Figure 1. The temperature was maintained at a certain elevated temperature, that is, 120, 150, and 180°C, respectively. The normal-

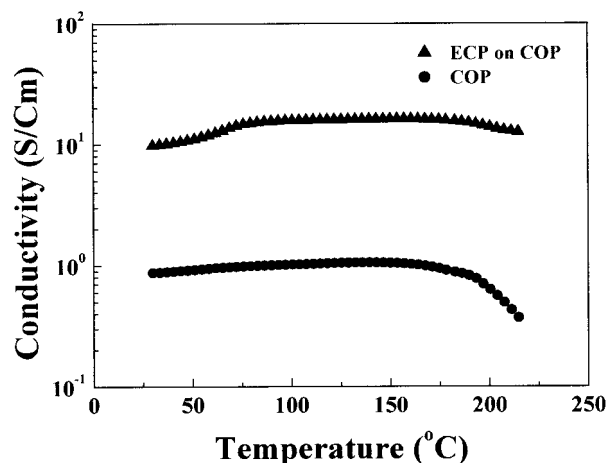


Figure 2 Electrical conductivity change of the composite fabrics from $T = 30$ – 210°C with heating rate of $10^\circ\text{C}/\text{min}$.

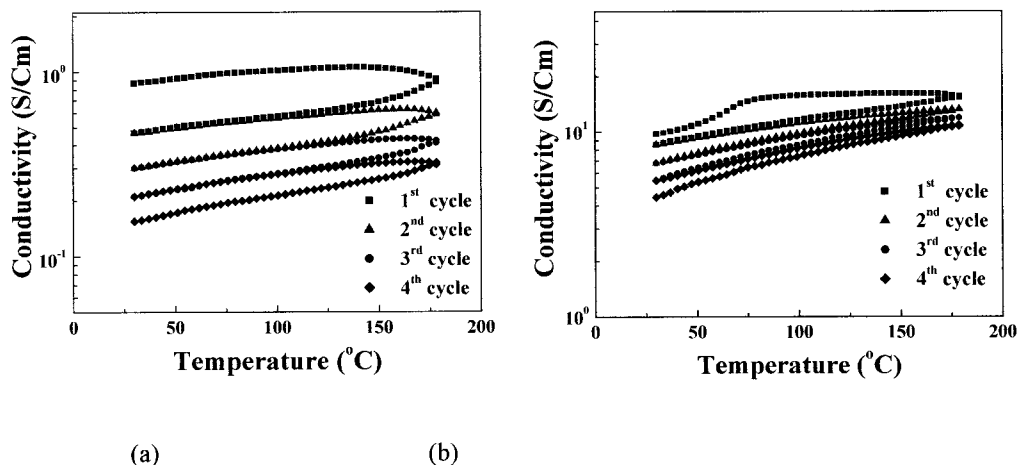


Figure 3 Temperature dependence of conductivity during cyclic heating and cooling between 30 and 180°C: (a) PPy-N prepared by COP; (b) PPy-N prepared by ECP on COP.

ized conductivities (σ_t/σ_0) are plotted as a function of time. The σ_t and σ_0 values represent the conductivity of the composites at the temperature of the experiment at a given time and at an initial time, respectively. For both the composite prepared by COP and that prepared by ECP on the COP fabric, the conductivity was retained at an almost constant level at 120°C for 600 min. However, the decrease in conductivity at higher temperatures showed very different tendencies: When the experimental temperature was 150 and 180°C, the conductivity of the COP composite abruptly decreased because of the dissociation of the dopant from the PPy chain. However, in the case of the ECP on the COP composite, the total loss of conductivity was less than 1 order of magnitude. The stability of the ECP on the COP composite was better than that of the COP composite, as the AQSA was able to strongly interact with the PPy main chain and was a larger dopant molecule than was the BSA.

The change in the electrical conductivity of the composite fabrics with temperature is shown in Figure 2. The temperature was increased from 30 to 210°C at a heating rate of 10°C/min. The conductivity of the COP composite reached a maximum at 140°C and then declined monotonically for temperatures up to 180°C. At this temperature, the conductivity was the same as was the initial value, but from then on, it decreased rapidly. On the other hand, for the ECP on the COP composite, the conductivity gradually increased with increasing temperature and reached its maximum conductivity at 153°C. Even though the

conductivity decreased above the maximum temperature, as in the case of the COP composite, it was greater than the initial value. This critical temperature to which conductivity increased means that there had to be molecular rearrangement on heating, which resulted in a molecular conformation favorable for electron delocalization. Also, it is supposed that the decrease in conductivity arose from the dissociation or evaporation of the dopant from the PPy chain. Using this point of view, the AQSA seems more thermally stable than the BSA.

Repeated heating-cooling experiments were performed over four cycles to further examine the conductivity temperature dependence. The conductivity of the COP composite changed and reached its initial value after the final temperature increase from 30 to 180°C, as mentioned previously. Therefore, the conductivity experiments were conducted in this temperature range. Figure 3 shows the temperature dependence of the conductivity during the four consecutive heating-cooling cycles. In the case of the COP composite, the conductivity at 30°C decreased considerably as the heating-cooling steps were repeated. However, in the case of the ECP on the COP composite, the decrease in the conductivity was low. In addition, the conductivity of the ECP on the COP composite increased substantially in the range from 70 to 80°C during the first heating stage, which was different from the result found for the COP composite. Interestingly, however, this phenomenon was not observed during the second, third, and fourth heating stages.

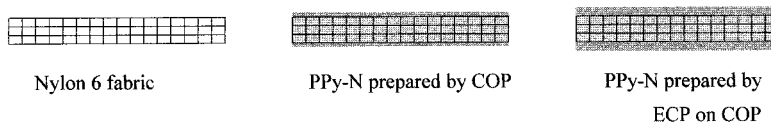


Figure 4 Schematics of the COP and ECP sequentially polymerized PPy-N fabric.

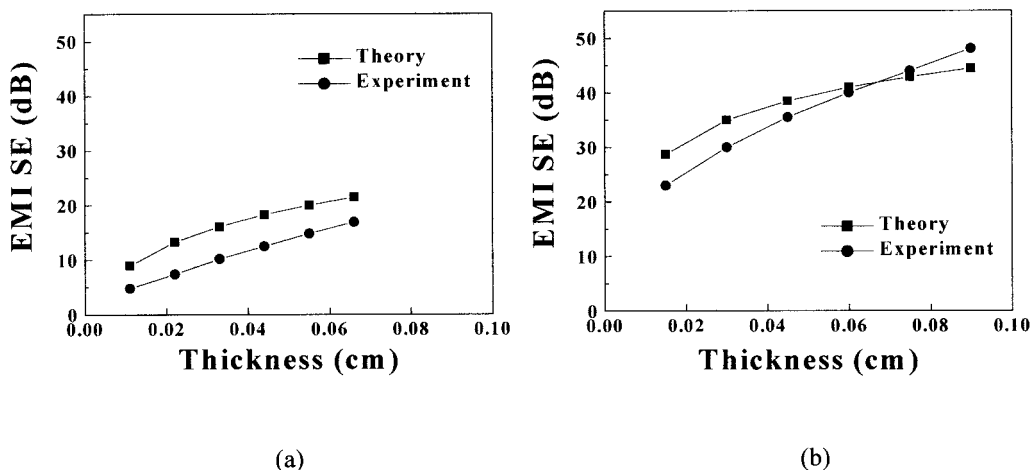


Figure 5 Effect of thickness on the theoretical and experimental EMI SE: (a) PPy-N prepared by COP; (b) PPy-N prepared by ECP on COP.

Therefore, the sudden increase in conductivity in this specific temperature range is assumed to be attributable to the aryl sulfonate dopant.¹⁶

EMI shielding characteristics of composite fabrics

The thickness of the composite fabric before and after the ECP process was approximately 0.011 and 0.015 cm, respectively. As presented in Figure 4, the resulting composite fabric had a triple-deck structure, which was composed of the chemically synthesized PPy layer sandwiched in the middle of the outer electrochemically synthesized PPy layers.

The effect of the composite thickness on the EMI SE was analyzed and the experimental SE of the composites was compared to the theoretical SE values based on a single-layer calculation. For a single layer, the theoretical EMI SE can be written as

$$\text{EMI SE (dB)} = 20 \log \left(1 + \frac{1}{2} \sigma d Z_0 \right) \quad (1)$$

where σ is conductivity; d , the thickness of the sample; and Z_0 , the free-space wave impedance, 377Ω .¹⁷ In this experiment, the stacking of composites prepared using the same method was used to achieve the increment in the composite thickness.

In Figure 5, the SE of the COP composite increased with an increasing composite thickness, and its EMI SE was 16 dB at a sample thickness of 0.066 cm. In the case of the COP composite, the experimental shielding value was lower than the theoretical value over the entire thickness range. The discrepancy between the experimental and theoretical values occurred because we calculated the theoretical SE values by assuming that the composite had no microvoids. However, the behavior of the ECP on the COP composite was dif-

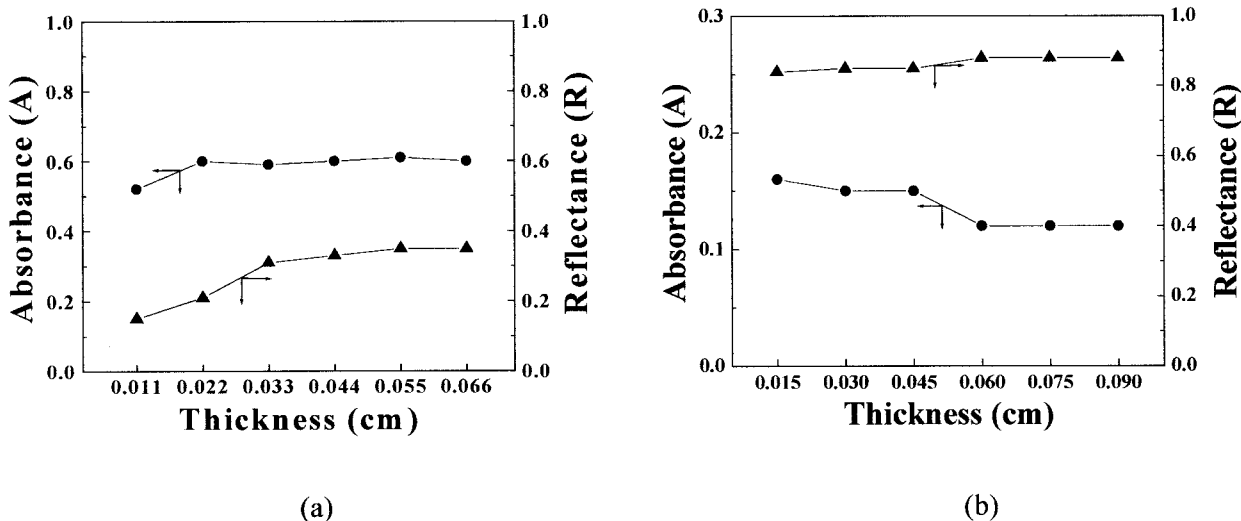


Figure 6 Effect of thickness on the absorbance and reflectance of (a) PPy-N prepared by COP and (b) PPy-N prepared by ECP on COP.

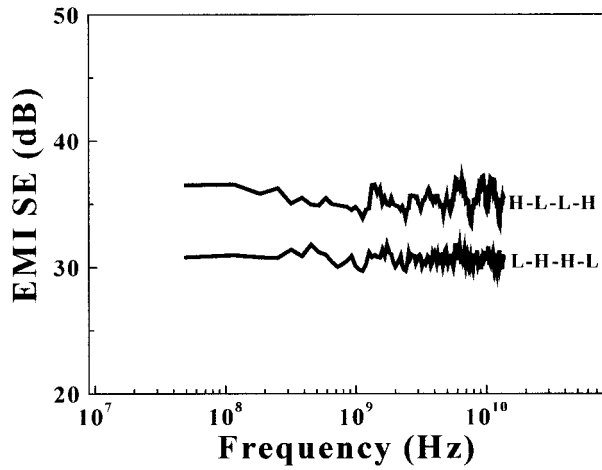


Figure 7 Effect of a multilayered type on the EMI SE of the composites.

ferent from that of the COP composite. The experimental and theoretical values were almost the same for an ECP on the COP composite of five stacked layers (0.075 cm thick). However, for a stack of six layers (0.09 cm thick), the experimental value was higher than the theoretical value. This result is thought to arise from an accumulation of multiple reflections caused by the PPy layers prepared by the COP method.¹⁸ In this sense, when the thickness and the conductivity of the PPy are supposed to be the same, the SE of PPy with a multilayer structure was superior to that having a single layer.

The S_{11} (S_{22}) and S_{12} (S_{21}) parameters (the S parameters) of a two-port network system represent the reflection and transmission coefficients, respectively. According to the analysis of S parameters, the transmittance (T), reflectance (R), and absorbance (A) can be described by

$$T = \left| \frac{E_T}{E_I} \right|^2 = |S_{12} \text{ (or } S_{21})|^2 \tag{2}$$

$$R = \left| \frac{E'_I}{E_I} \right|^2 = |S_{11} \text{ (or } S_{22})|^2 \tag{3}$$

where E'_I is the reflected electric field and A is obtained by using the relation $T + R + A = 1$.

The effect of the thickness on the EMI shielding characteristics of the composites is presented in Figure 6. The absorbance of the COP composite increased with the thickness and reached a maximum at approximately 0.6. The reflectance of the COP composite increased with the thickness and reached a maximum at approximately 0.35. In the case of the ECP on the COP composite, the absorbance decreased with the thickness and reached a minimum at approximately 0.12. The reflectance increased with the thickness increment and reached a maximum at approximately 0.88. The EMI shielding characteristics of the composite dominated the absorbance below 20 dB and the reflectance above 20 dB.

We conducted an experiment to investigate the effect of an array of highly conducting (H) and low conducting (L) layers on the shielding effect, and we designed composites composed of multilayers with various conductivities. In this experiment, the L layer was a composite prepared by COP (0.87 S/cm, 5 dB) and the H layer was a composite prepared by ECP on COP (9.8 S/cm, 24 dB), respectively. The SE of the composites composed of an H-L-L-H type and an L-H-H-L type are compared in Figure 7. The SE of the H-L-L-H-type composite was higher than that of the L-H-H-L-type composite with the value of 37 dB. Also, this indicates that the SE of the H-H-H-H-type composite and that of the H-L-L-H-type composite

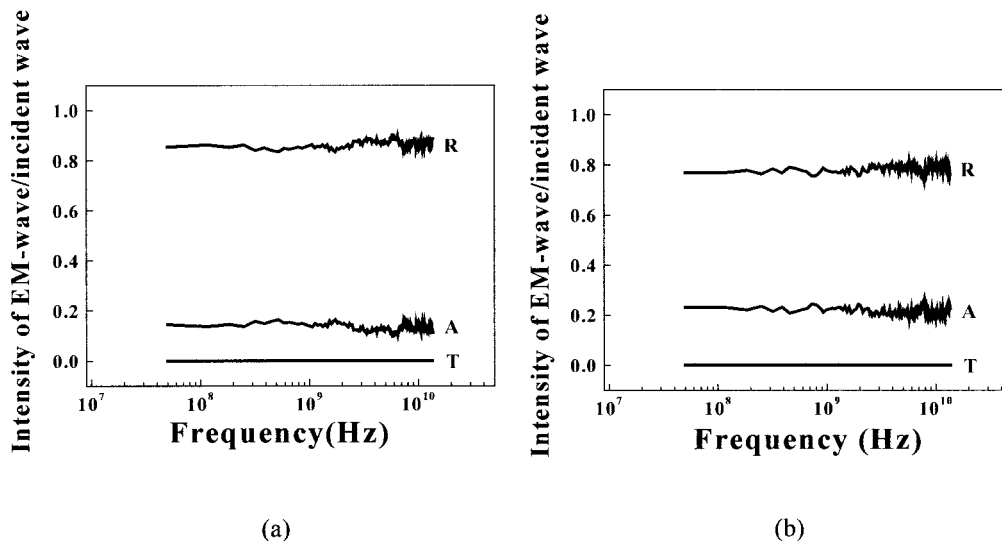


Figure 8 Effect of a multilayered type on the EMI shielding characteristics of composites (a) H-L-L-H; (b) L-H-H-L.

were almost the same. Figure 8 shows that the reflectance of H-L-L-H-type composite was higher than that of the L-H-H-L-type composite. It was assumed that the higher conductivity layer (H) has a conductivity twice that of the L-H-H-L-type composite. However, in the case of the H-L-L-H-type composite, multiple reflections from the existence of the L layers, having a different conductivity, increased together with the previously mentioned effect.¹⁸

We studied the effect of the increment in L layers on the EMI SE of H-L-L-H-type composites. In Figure 9, the SE of an H-L-L-L-L-H-type composite was approximately 42 dB. The SE of an H-H-H-H-H-type composite and an H-L-L-L-L-H-type composite would be expected to be nearly the same as those of the previous results above. However, the results of the SE of the H-H-H-H-H-type composite showed that the SE value was higher than that of the H-L-L-L-L-H-type composite. The EMI shielding characteristics of the H-L-L-L-L-H-type composite is shown in Figure 10. The reflectance of the H-L-L-L-L-H-type composite was lower than that of the H-L-L-H-type composite. This shows that an increment in L layers has a limitation in the improvement of the SE value. However, an L layer may control the absorbance and reflectance EMI shielding characteristics.

CONCLUSIONS

PPy-N composite fabrics for use in EMI shielding were prepared by COP and ECP. The ECP on the COP composites showed a higher stability in their conductivity than those prepared by COP. The conductivity of ECP on the COP composite had an almost constant value at 180°C for 600 min. The change of the composites' conductivity with cyclical heating and cooling was explained by the thermal stability of the dopant

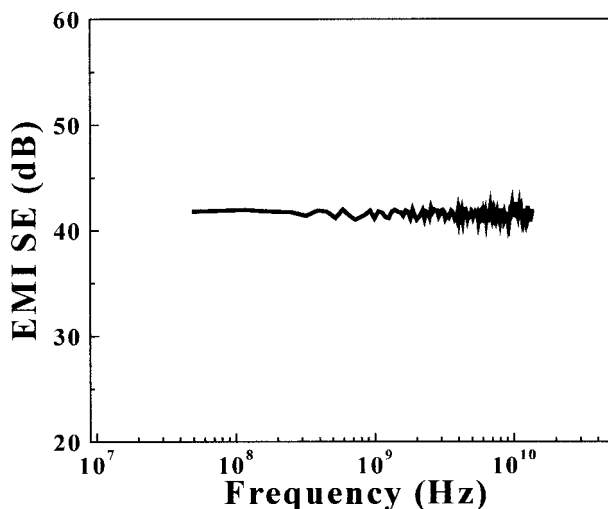


Figure 9 Frequency dependence of the EMI SE for the H-L-L-L-L-H-type composite.

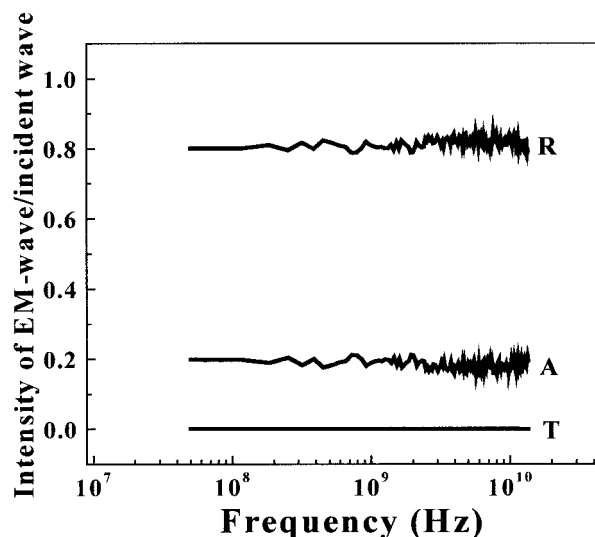


Figure 10 EMI shielding characteristics of the H-L-L-L-L-H-type composite.

and the rearrangement of the PPy main chain. The EMI SE and the ratio of the absorbance and the reflectance of the composite could be controlled by an array of high-conducting and low-conducting layers. The maximum EMI SE of the composite achieved was approximately 40 dB in the measured frequency range. The EMI shielding characteristics of the composites showed that absorption dominated the total EMI SE below 20 dB and that reflectance dominated the total EMI SE above 20 dB.

References

- Oh, K. W.; Kim, D. J.; Kim, S. H. *Polymer (Korea)* 2001, 25, 302.
- Joo, J.; Epstein, A. J. *J Appl Phys Lett* 1994, 65, 2278.
- Kuhn, H. H.; Child, A. D.; Kimbrell, W. C. *Synth Met* 1995, 71, 2139.
- Wang, L. X.; Li, X. G.; Yang, Y. L. *React Func Polym* 2001, 47, 125.
- Li, H. H.; Shi, C. Q.; Ye, W.; Li, C.; Ling, Y. Q. *J Appl Polym Sci* 1997, 64, 2149.
- Oh, K. W.; Kim, S. H.; Kim, E. A. *J Appl Polym Sci* 2001, 81, 684.
- Oh, K. W.; Hong, K. H.; Kim, S. H. *J Appl Polym Sci* 1999, 74, 2049.
- Im, S. S.; Byun, S. W. *J Appl Polym Sci* 1994, 51, 1221.
- Jang, S. H.; Byun, S. W.; Kim, S. H. In *Sixth Asian Textile Conference 2001*; p 6.
- Lee, Y. K.; Cho, J. C. *Polymer (Korea)* 2000, 24, 276.
- Heisey, C. L.; Wightman, J. P.; Pittman, E. H.; Kuhn, H. H. *Text Res J* 1993, 63, 247.
- Bhadani, S. N.; Gupta, S. K. S.; Sahu, G. C.; K, M. *J Appl Polym Sci* 1996, 61, 207.
- Iroh, J. O.; Williams, C. *Synth Met* 1999, 99, 1.
- Park, Y. H.; Choi, S. H.; Song, S. K.; Miyata, S. *J Appl Polym Sci* 1992, 45, 843.
- Jang, S. H.; Byun, S. W.; Kim, S. H.; Joo, J.; Lee, J. Y.; Jeong, S. H. *J Kor Fiber Soc* 2002, 39, 217.
- Takeoka, S.; Hara, T.; Yamamoto, K.; Tsuchida, E. *Chem Lett* 1996, 253.
- Colaneri, N. F.; Shacklette, L. W. *IEEE Trans Instru Meas* 1992, 41, 291.
- Joo, J.; Lee, C. Y. *J Appl Phys* 2000, 88, 513.