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Electromagnetic Interference Shielding Effectiveness of New Conducting Polymer Composite

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Electrical conductivity and shielding effectiveness (SE) of conductive polymer composite of polypyrrole-chitosan (PPy-CHI) have been studied. It was shown that chitosan can improve electrical and thermal properties of polypyrrole. The applicability of PPy-CHI composite films to the electromagnetic wave shielding in the microwave frequency range from 8 to 12 GHz were investigated. The SE of the composite films had a strong dependence on chitosan content. The SE of the composite films was obtained by Simon formalism. Comparison of the experimental and theoretical values revealed good correspondence of the shielding of the composite films at high conductivity and frequency.

Keywords: Polypyrrole, chitosan, thermal diffusivity, shielding effectiveness, Simon formalism

1 Introduction

Transmission of electromagnetic waves can cause electromagnetic interference (EMI), degradation and interception of the performance of electronic or electrical devices and can be harmful to the human body. Shielding is the process of limiting the flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material. Total EMI shielding effectiveness (EMI SE) of a material is the sum of shielding effectiveness (SE) resulting from reflection, absorption and multiple internal reflection. It means that a shield is a barrier to the transmission of electromagnetic waves (1).

The requirements for reflection and absorption of the radiation by the shield are the existence of mobile charge carriers (electrons or holes) and electric and/or magnetic dipoles, respectively which interact with the electromagnetic fields in the radiation. In the materials with high conductivity (high value of charge carrier), shielding occurs mainly through the reflection, while in the materials with high value of the dielectric constant and magnetic permeability, shielding through absorption is significant. Reflections at various surfaces or interfaces in the shield have been known as multiple reflections. This mechanism requires the presence of a large surface area (porous or foam material) or interface area in the shield (composite material containing filler) (2). When the distance between the reflecting surfaces or interfaces is large compared to the skin depth the shielding by multiple reflections can be ignored (same as conducting polymer without filler) and the shielding effectiveness (SE) can be expressed by the following equation (3).

$$\mathrm{SE} = \mathrm{R} + \mathrm{A} \tag{1}$$

Where R is the reflection loss of the electromagnetic wave, and A is the absorption loss of the energy of the electromagnetic wave. Even though a study on the composite with small filler shows that due to the skin effect in these materials shielding by multiple reflections is significant and they provide higher shielding (3–5).

Skin effect is a phenomenon in which high frequencies of the electromagnetic radiation can penetrate only the near surface region of an electrical conductor and by increasing depth in to the conductor, the electric field of electromagnetic wave penetrating a conductor drops exponentially.

The depth at which the field drops to $1/e$ of the incident value is called the skin depth, which is given by Equation 2:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{2}$$

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Where δ = skin depth (m), f = frequency (Hz), μ = magnetic permeability (H m^{-1}) and σ = electrical conductivity in Ω^{-1} m^{-1}. The skin depth decreases with increasing conductivity (1). Hence, absorption decreases with the increase in conductivity while the reflection increases.

The EMI shielding effects of electroconductive composites can be estimated by the Simon formalism (3):

$$SE = 50 + 10\log(\rho f)^{-1} + 1.7t(f/\rho)^{1/2} \quad (3)$$

Where SE is in dB, ρ is the volume resistivity (Ω cm) at room temperature, t is the thickness of the sample (cm), f is the measurement frequency (MHz) respectively. The first two terms estimate the shielding effect by reflection (R_e) and the third term represents the shielding by absorption (A_b). In this empirical equation, the effect of multiple reflections has been omitted. However, in the composite materials, having conductive filler with a small size, this effect is significant (3).

In many applications, EMI shielding by absorption rather than reflection is more important. Metals such as steel, copper, aluminium and nickel are the most common materials for shielding. Due to their free electrons and shallow skin depth, EMI shielding in these materials is mainly through the surface reflection, while EMI shielding in electrically conducting polymers is through both reflection and absorption and can be enhanced by controlling electrical conductivities or the dielectric constants. Hence, conducting polymers exhibit a significant advantage over the metallic shielding materials. Further more metals compared to conducting polymer have shortcomings of heavy weight, corrosion and physical rigidity (6).

Due to processability and low density, the composite materials having conductive filler with a small unit size of the filler are attractive for shielding. Skin depth in these materials can be enhanced by decreasing the size of the filler (7). Composites material containing conductive filler are widely used for the shielding application. Park et al. (8) investigated the applicability of glass fabric/epoxy composites containing conductive multi-walled carbon nanotubes (MWNT) to electromagnetic wave shielding enclosures and Lee, et al. (9) studied the electromagnetic characteristics of MWNT-filled glass/epoxy plain-weave composites.

Conducting polymers don't require conductive filler in order to provide shielding; so that they may be used with or without filler, but they have poor processability and mechanical properties.

Due to high conductivity, good environmental stability and easy synthesis of polypyrrole, this conducting polymer is fit to use in EMI shielding. Some works about using this material in the textiles are reported (10). A textile/PPy composite with EMI SE about 36 dB over a frequency range of 50 MHz–1.5 GHz was reported by Kim (2). In this study, chitosan as a biodegradable, biocompatible, nontoxic and low-cost polymer (11) has been used to improve mechanical properties of polypyrrole. Heat transfer is one of the requirements of the material used in some electronic devices. Due to its importance, the thermal diffusivity of the PPy-CHI composite films was also studied.

2 Experimental

2.1 Materials

Chitosan (CHI) was obtained from a local company with 88% degree of deacetylation. Pyrrole (Py) was provided by Acros Organic and *p*-toluene sulfonate was supplied by Fluka. A typical three-electrode electrochemical cell arrangement was used with a saturated calomel electrode (SCE), a carbon rod and an indium-tin oxide (ITO) glass as the reference, counter and working electrode, respectively.

2.2 Methods

Chitosan acetate solutions were prepared by dissolving chitosan powder (w gram) in 1% acetic acid (v ml) and then mixed with pyrrole and *p*-TS in 1% acetic acid. The anodic potential of the working electrode was measured as +1.2 volt against a saturated calomel electrode (SCE). Electrochemical deposition of PPy and CHI was performed using a potentiostat (Model: PS 605, USA).

All polymers were electrochemically prepared in a solution containing 0.3 M pyrrole (pre-distilled) and 0.1 M *p*-TS dopant and various concentrations of CHI in acetic acid at room temperature. For comparison purposes, PPy film without chitosan was prepared.

2.3 PolymerCharacterization

The PPy-CHI conducting polymer composite films were characterized by conductivity measurement, thermal diffusivity and EMI shielding effectiveness. The electrical conductivity was measured at room temperature by the standard four probe technique and expressed as the specific volume conductivity (S cm^{-1}). The EMI SE of the PPy-CHI and PPy films were measured using network analyzer (Hewlett Packard), 8752C network analyzer, in the frequency range of 8–12 GHz. The analyzer was calibrated before using.

The samples of PPy-CHI composite films were sandwiched by clamping them between two waveguide-to-coaxial transducers and then the reflection and transmission coefficients of the films were obtained at frequencies of 8-12 GHz. R_e and T_r were obtained by the measurement of S-parameters, S_{11} (or S_{22}) and S_{12} (or S_{21}) for the reflection and the transmission, respectively and the absorbance (A_b) calculated using the following Equation 4:

$$A_b = 1 - T_r - R_e \quad (4)$$

R_e and T_r are the square of the ratio of reflected (E_r) and transmitted (E_t) electric fields to the incident electric field

(E_i) respectively, as follows (Eqs. 5 and 6):

$$R_e = \left|\frac{E_r}{E_i}\right|^2 = |S_{11}(\text{or}S_{22})|^2 \quad (5)$$

$$T_r = \left|\frac{E_t}{E_i}\right|^2 = |S_{21}(\text{or}S_{12})|^2 \quad (6)$$

EMI SE value expressed in dB was calculated from the ratio of the incident to transmitted power of the electromagnetic wave as follows (Eq. 7):

$$SE = 10\log\left|\frac{P_1}{P_2}\right| \text{(Decibels; dB)} \quad (7)$$

Where P_1 and P_2 are the incident and transmitted power, respectively (4, 12). The open photoacoustic cell (OPC) technique was used for thermal diffusivity measurements. The importance of thermal diffusivity as a physical quantity to be measured is due to the fact that, like the optical-absorption coefficient, it represents an intrinsic property for each material (13). The heat transfer was obtained by measuring the thermal diffusivity α, a quantity defined by Equation 8:

$$\alpha = \frac{k}{\rho c} \quad (8)$$

Where k, ρ, and c are the thermal conductivity, density and specific heat at constant pressure, respectively.

3 Results and Discussion

3.1 Electrical Conductivity of the Composite Films

The electrical conductivity of the conductive composite films of PPy-CHI vs. CHI concentration is shown in Figure 1. All of films prepared from 0.3 M Py and 0.1 M *p*-TS. The applied potential was +1.2 volt against SCE. Each composition of PPy-CHI was prepared 3 times and the average of conductivities was taken. The electrical conductivity was found to increase as the CHI content increased. The conductivity increased from 33.5 Scm^{-1} to 69.1 Scm^{-1} with an increase in CHI concentration in the solution from 0.1% to 0.7% (w/v). Since the electrical conductivity increases as the conjugation length of the polymer increases (14), the presence of CHI can be linked to increase the conjugation length. As Yang et al. (15) reported, chitosan is a useful steric agent with amino and hydroxyl groups to promote the interaction between the pyrrole monomers and its oligomers. They used chitosan as stabilizer to prepare Hollow nanometer-sized polypyrrole capsules. The optimum concentration of CHI for the best conductivity was 0.7% (w/v) but after that, the conductivity decreased to 33.5 $Scm^{-1}$with further increase in CHI concentration. This is due to the fact that in the concentrations more than 0.7% (w/v) of CHI, in highly viscose solution, the rate of oxidation and polymerization is very slow and the amount of deposited polymer is much lower which leads to low conductivity.

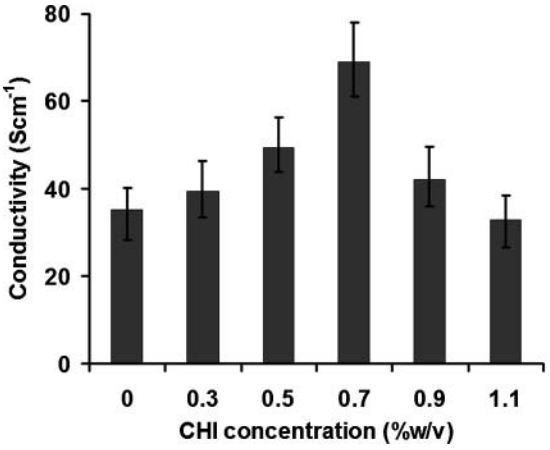

Fig. 1. Electrical conductivity of conducting polymer composite films vs. CHI concentration (0% of CHI represents of the PPy without CHI).

3.2 Thermal Diffusivity

There is a good correlation between thermal diffusivity and electrical conductivity (Fig. 2). The thermal diffusivity increased from 4.29×10^{-8} to 4.17×10^{-7} (m^2s^{-1}) as the chitosan content increased from 0.1% to 0.7% w/v, and then showed a decreasing trend with a further increase in chitosan concentration. When the conjugation chain length of the polymer increased, the free movement of charge carriers increased and the electrical conductivity increased. These results indicate that the thermal diffusivity of the PPy-CHI composite films relates to the electron migration in the conjugation chain length (16).

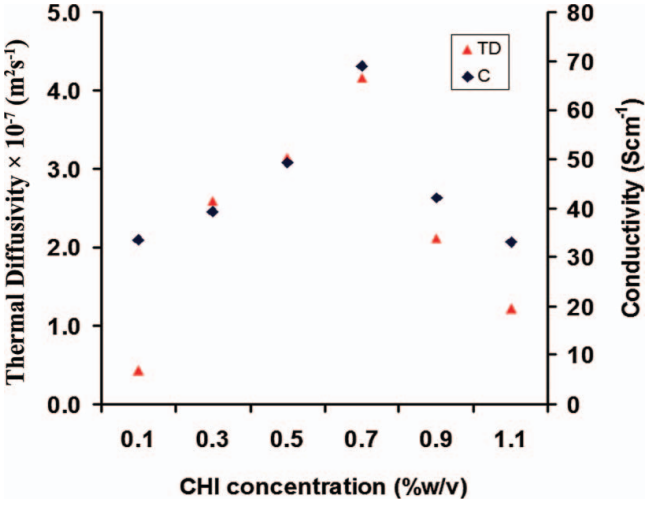

Fig. 2. Correlation between thermal diffusivity (TD) and conductivity (C) of the composite films vs. CHI concentration.

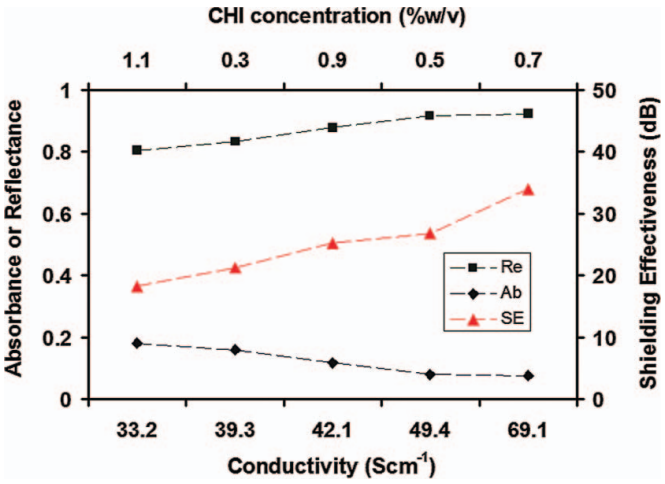

Fig. 3. The shielding effectiveness (SE), absorbance (A_b) and reflectance (R_e) of PPy-CHI composite films with various electrical conductivity and different concentration of chitosan.

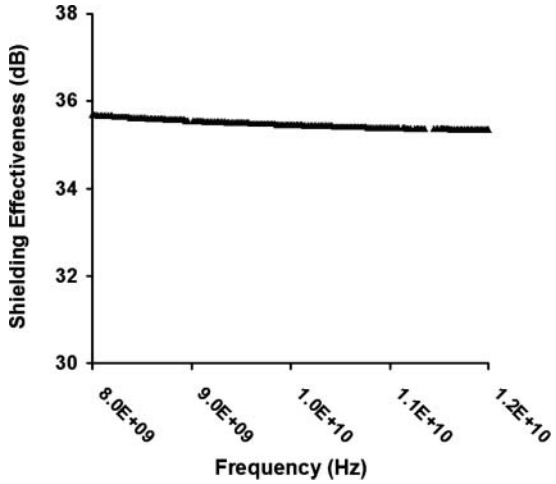

Fig. 4. Variation of the shielding effectiveness of the composite film (with conductivity of 69.1 Scm^{-1}) with electromagnetic wave frequency according to the theoretical calculation.

3.3 Electromagnetic Interference Shielding Effectiveness

The average values of SE were obtained for the composite films by network analyzer, which were almost constant in the studied frequency range. The results of SE, absorbance and reflectance over the frequency range are plotted as a function of the conductivity and CHI content in Figure 3. In all of the compositions, concentration of py and *p*-TS were 0.3 and 0.1 molar, respectively (the applied voltage was 1.2 volt against SCE). It shows that EMI SE gradually increased from 21.2 dB to 33.9 dB with the increase in the conductivity and then decreased to 18.3 dB which is due to the decrease in conductivity. The increase in EMI SE with an increase in electrical conductivity results from shielding by reflection rather than absorption. This is due to the fact that the sample with high conductivity has more mobile charge carriers that can interact with the electromagnetic fields in the radiation, hence shielding by reflection increases. The decrease of A_b must be due to shallower skin depth of the composite with higher electrical conductivity. The relationship between EMI SE and electrical conductivity of the PPy-CHI composite films is in good agreement with the results obtained by others (1, 17).

The electromagnetic interference shielding effectiveness of PPy-CHI composite film (with conductivity of 69.1 Scm^{-1}) was around 33.9 dB, while an average shielding effectiveness of around 19.8 dB has been offered by the PPy film without CHI. Thus, it shows that when PPy is incorporated with CHI forming PPy-CHI composite, is capable of the offering higher EMI SE. Shielding effectiveness of the composite film (with conductivity of 69.1 Scm^{-1}) has been calculated by the Simon equation also, and the results are shown in Figure 4.

The reflectance, absorbance and SE calculated according to the Simon equation (labled as SE_{emp}) and the experimental results of SE (labeled as SE_{exp}) are listed in Table 1. As indicated by the equation, the R_e increased with the increase in conductivity and is in agreement with the experimental results. The experimental and theoretical values of absorption are not so coincidences with each other. It shows this empirical equation can not predict only absorption.

For all the composite films, the experimental SE is lower than the empirical value calculated from Equation 3 for the studied frequency range. Since the empirical equation considers the SE from reflection and absorption, we can

Table 1. The comparison of experimental results with that obtained by theoretical calculation in two different frequencies

		8000MHz				*12000 MHz*		
CHI % (w/v)	*C(Scm^{-1})*	*$SE_{(exp)}$ (dB)*	*$R_{e(emp)}$ (dB)*	*$A_{b(emp)}$ (dB)*	*$SE_{(emp)}$ (dB)*	*$R_{e(emp)}$ (dB)*	*$A_{b(emp)}$ (dB)*	*$SE_{(emp)}$ (dB)*
0.3	39.3	21.23	26.91	5.24	32.15	25.15	6.42	31.57
0.5	49.4	26.91	27.89	6.41	34.31	26.14	7.85	33.99
0.7	69.1	33.90	29.34	6.32	35.66	27.60	7.74	35.34
0.9	42.1	25.34	27.18	7.40	34.58	25.45	9.06	34.51
1.1	33.5	18.34	26.18	6.86	33.04	24.46	8.40	32.86

C = Conductivity, A_b = Absorbance, R_e = Reflection, SE = Shielding effectiveness, emp = empirical, exp = experimental

get results that SE from multiple reflections in this material is very small and Simon formulism, which is an estimated equation, predicts SE in ideal conditions. Hence, the SE that is obtained for all polymers using this equation is higher than that obtained by experiment.

At high conductivity, the *SE* obtained by measurement approximately corresponds to that obtained by theoretical calculation. The accuracy of the values obtained for reflection using this formula is higher than that for absorption. Hence, in high conductivity, which SE is mainly from reflection, shielding effectiveness of the composites can be predicted using this empirical equation. Another result can be obtained from this experiment is that in the high-frequency range (12000 MHz), which is generally used, the experimental and theoretical *SE* values correspond more. These results are in good agreement with others (1, 3).

4 Conclusions

CHI can improve EMI SE, electrical conductivity and thermal diffusivity of the PPy film. The SE and reflection increased with an increase in conductivity, while absorption decreased. The decrease of absorption must be due to shallower skin depth of the composite with higher electrical conductivity.

At high frequencies and conductivity, the SE obtained by measurement approximately corresponds to that obtained by theoretical calculation, so that the shielding effectiveness of the composites can be predicted in conductive polymer composites with high conductivity at high frequency using empirical equation.

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