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ELECTRICAL AND SHIELDING PROPERTIES OF CONDUCTIVE POLYMER COMPOSITE MATRIX WITH CHITOSAN

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ABSTRACT

The polypyrrole-chitosan (PPy-CHI) composite films formed by electrochemical polymerization were studied by electrical and mechanical techniques. The electromagnetic interference shielding effectiveness (EMI SE) at the frequencies range from 8-12 GHz was also studied. It is shown by electrical conductivity measurement and DMA (dynamic mechanical analysis) that the enhanced conductivity and mechanical properties of the prepared films are due to the presence of CHI in the composite film. Most of the composite films had more than 98% shielding of electromagnetic energy. The EMI SE shown through reflection and absorption increased with the increase in conductivity and relative shielding efficiency by reflection and absorption can be easily controlled by the electrical conductivity.

INTRODUCTION

Since polypyrrole can be prepared easily by electrochemical polymerization on electrodes, numerous works have been made on the characterization and finding application of this polymer in sensors, electronic and optical devices, etc. Due to high conductivity, good environmental stability and easy synthesis of polypyrrole, this conducting polymer is capable to use in EMI shielding. Some works about using this material in the Textiles are reported [1, 2]. A textile/PPy composite with EMI SE about 36 dB over a frequency range of 50 MHz–1.5 GHz was reported by M.S. Kim [3].

Shielding is the process of limiting the flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material. Transmission of electromagnetic waves may cause electromagnetic interference (EMI) as well as can be harmful to human body.

EMI shielding occurs by the reflection and/or absorption of electromagnetic radiation by a material, which acts as a shield against the penetration of the radiation through it.

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In the materials with high conductivity (high value of charge carrier) shielding occurs mainly through the reflection [4]. Reflections at various surfaces or interfaces in the shield have been known as multiple reflections. In the composites with small filler (high surface area) due to the skin effect (the phenomenon in which high-frequency electromagnetic radiation can penetrate only the surface region of an electrical conductor) shielding by multiple reflections mechanism is significant. The skin depth decreases with increasing conductivity. Hence absorption decreases with the increase in conductivity while the reflection increases [5, 6].

Metals are the most common materials for shielding. In these materials shielding 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. Furthermore, compare to the metals, conducting polymers have no shortcomings of heavy weight, corrosion and physical rigidity.

The composite materials having conductive filler with a small unit size of the filler are attractive for shielding [7, 8]. Skin depth in these materials can be enhanced by decreasing the size of the filler. Conducting polymers do not require conductive filler in order to provide shielding, hence they may be used with or without filler but they have poor processability and mechanical properties. In this present study, we used CHI as a conventional polymer to enhance the mechanical properties of conducting polypyrrole with the aim of producing a new composite of conducting polymer for use in the EMI shielding.

EXPERIMENTAL METHOD

Materials

Chitosan (CHI) was obtained from a local company with 88% degree of deacetylation, Pyrrole (Py) monomer 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. The composite films were produced from an aqueous solution containing pyrrole monomer, *p*-toluene sulfonate dopant and chitosan polymer.

Methods

Various amounts of chitosan powder (w) were dissolved in 1% acetic acid solution (v). The prepared chitosan acetate solutions were mixed with PPy and *p*-TS in 1% acetic acid solution. Electrochemical deposition of PPy and CHI was performed using a potentiostat (Model: PS 605, USA). The conducting polymer composite films with different concentration of Py, CHI, *p*-TS and different applied voltage were prepared.

Polymer Characterization

The PPy-CHI conducting polymer composite films were characterized by conductivity

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measurement, dynamic mechanical analysis (DMA) and EMI shielding effectiveness. The electrical conductivity was measured at room temperature by the standard Four Point Probe technique and expressed as the specific volume conductivity (Scm^{-1}). The dynamic mechanical analysis was done by using Perkin Elmer (Pyris Diamond). The EMI SE of the PPy-CHI and PPy films were measured using Agilent technologies N5230A network analyzer (Hewlett Packard), in the frequency range of 8-12 GHz.
The samples of Polypyrrole-Chitosan (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 and the absorbance (A_b) calculated using the following Eq (1)

$$A_b = 1 - T_r - R_e \qquad (1)$$

EMI SE value expressed in dB was calculated from the ratio of the incident to transmitted power of the electromagnetic wave as following Eq. (2):

$$SE = 10\log\left|\frac{P_1}{P_2}\right| \qquad \text{(decibels, dB)} \qquad (2)$$

Where P_1 and P_2 are the incident and transmitted power, respectively [9, 10].

RESULTS AND DISCUSSION

Electrical conductivity of the composite films

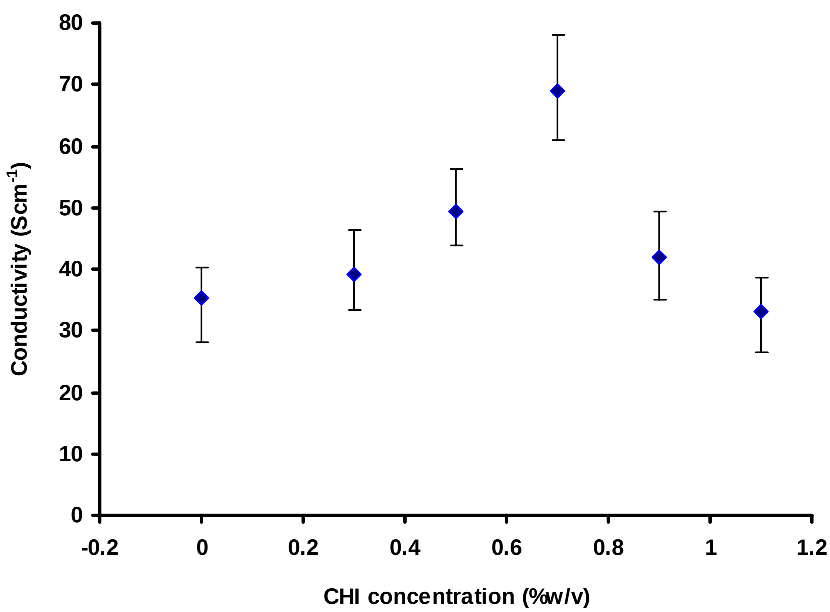

Figure 1: Electrical Conductivity of PPy-CHI composite films versus CHI concentrations 0 of CHI represents of PPy without CHI.

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Each composition of PPy-CHI was prepared 3 times and the average conductivity was taken. The electrical conductivity of the composite film of PPy-CHI prepared from solution containing 0.3 M Py and 0.1 M *p*-TS versus CHI concentration is shown in Figure 1. The applied potential was 1.2 volt against SCE. The conductivity increased from 33.5 Scm^{-1} up 69.1 Scm^{-1} with an increase in CHI concentration. The presence of CHI can be linked to increase the conjugation length since the electrical conductivity increases as the conjugation length of the polymer increases [11]. Maximum conductivity was obtained from the film prepared using 0.7% CHI (69.1 Scm^{-1}). Later, the conductivity dropped to 33 Scm^{-1} with further increase in CHI concentration. This is due to the fact that 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.

Dynamic mechanical analysis (DMA)

Figure 2 shows the change of storage modulus (E′) of the PPy-CHI composite films with the increase in temperature. The storage modulus of the films were measured in the temperature range of 25 to 250 °C with a heating rate of 2 °C per minute and at a frequency of 1 Hz. The PPy film without CHI had a very low E′ value in the measured temperature range but when CHI is combined with PPy, the storage modulus (E′) increases revealing the higher elastic property of the PPy-CHI composite film due to the addition of CHI in the polypyrrole structure. In addition, this is also an evidence of incorporating chitosan in the polypyrrole structure.

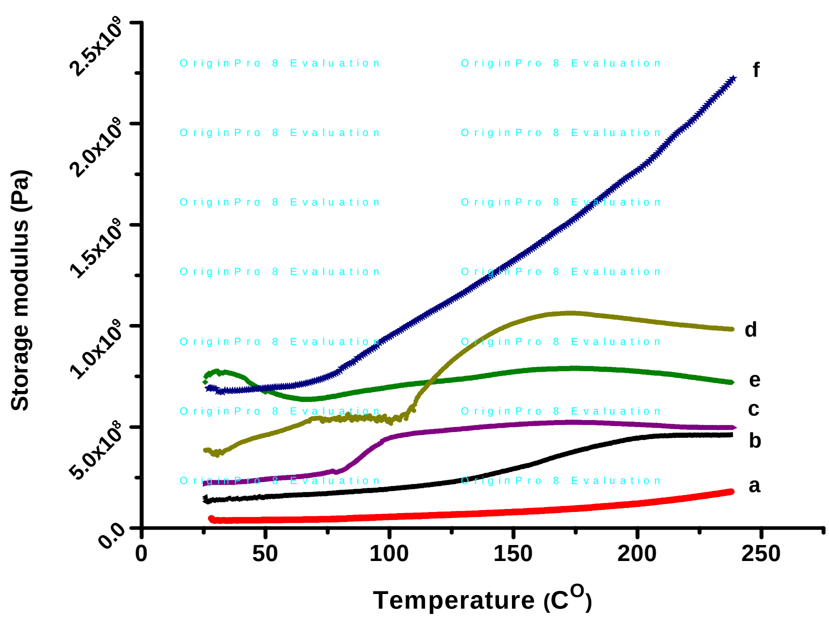

Figure 2: Temperature dependence of storage modulus (E′) for the (a) PPy and PPy-CHI films with (b) 0.3%, (c) 0.5%, (d) 0.7%, (e) 0.9%, (f) 1.1% w/v of CHI

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Electromagnetic Interference Shielding Effectiveness

The effects of different parameters and condition on the EMI SE of the PPy-CHI composite films in the microwave frequency range of 8-12 GHz were investigated. The reflection, transmission coefficients and shielding effectiveness of the film prepared of 0.7% (w/v) CHI, 0.1 M *p*-TS, 0.3 M Py at 1.2 volt against SCE (σ=69.1 Scm^{-1}, SE=33.9 dB) are shown as an example in figure 3 and 4.

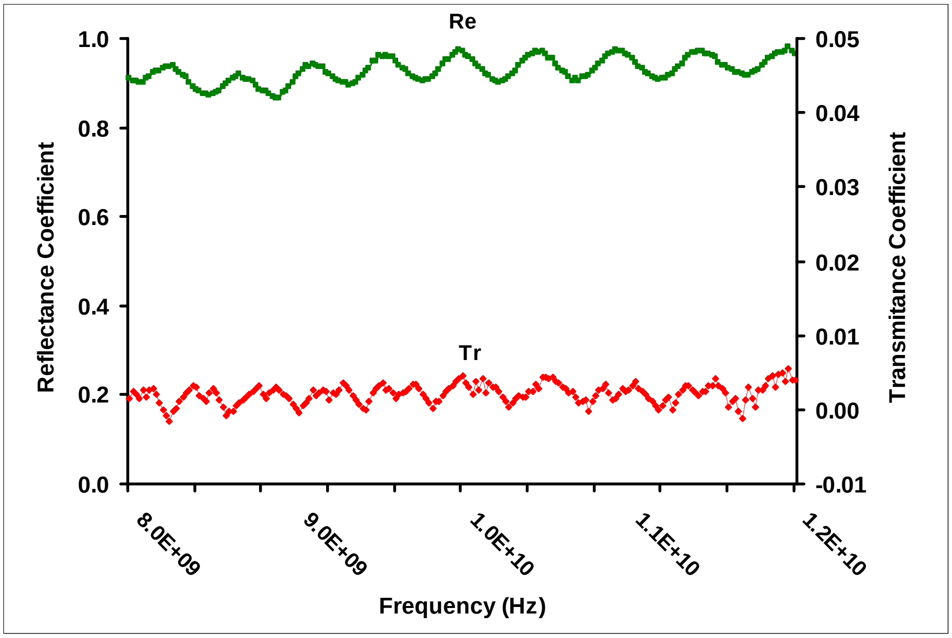

Figure 3: Reflectance and Transmittance of PPy-CHI composite film (σ=69.1 S/cm) in the frequency range of 8-12 GHz.

As shown in Figure 3 the average of reflection and transmission of the polymer over the study frequency are almost constant.

The results of transmission, reflection, absorption, SE and total attenuation of the PPy-CHI composite films prepared at various concentrations of chitosan and PPy without chitosan have been shown in the Table 1. In all of the compositions, concentration of py and *p*-TS were 0.3 and 0.1 molar respectively and the applied voltage was 1.2 volt against SCE. It shows that the total attenuation increased with the increase in conductivity. Most of the composite films showed more than 98% shielding of electromagnetic energy (total attenuation). It was found that in all cases SE from reflection is much larger than absorption. As shown in this Table when PPy is incorporated with CHI forming PPy-CHI composite films, is capable of the offering higher electromagnetic interference (EMI) shielding effectiveness (SE). The relationship between EMI SE and electrical conductivity of the PPy-CHI composites is in good agreement with the results obtained by others [8, 12, 13].

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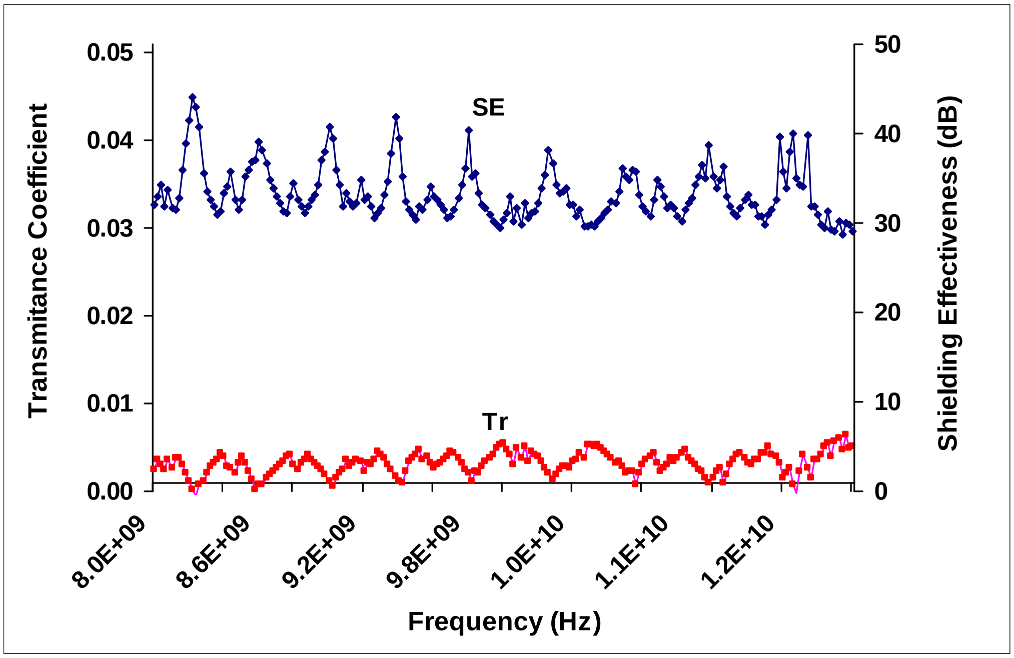

Figure 4: Shielding effectiveness and Transmittance of PPy-CHI composite film (σ=69.1 S/cm) in the frequency range of 8-12 GHz.

Table 1: Conductivity, Tr, Ab, Re and EMI SE of the PPy-CHI composites films with various concentrations of CHI and PPy without CHI

CHI conc.(%w/v)	C(Scm^{-1})	Tr (%)	Ab (%)	Re (%)	Total Atten	SE (dB)
0.3	39.3	0.75	16.05	83.2	99.25	21.2
0.5	49.4	0.20	8.09	91.7	99.79	26.9
0.7	69.1	0.04	7.56	92.4	99.96	33.9
0.9	42.1	0.29	11.91	87.8	99.71	25.3
1.1	33.5	1.50	18.12	80.4	98.52	18.3
PPy	35.2	1.01	16.21	82.8	99.01	19.8

C=Conductivity, Tr=Transmittance, Ab=Absorbance, Re=Reflection, Atten=Attenuation, SE=Shielding effectiveness (from Ab and Re), All of the films prepared from solution containing 0.3 M Py, 0.1 M *p*-TS at 1.2 volt (vs SCE)

As it is shown in Table 1, EMI SE gradually increased from 21.2 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 increase in electrical conductivity results

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from shielding by reflection rather than absorption. In other words, shielding effectiveness by reflection increased with the increase in conductivity, while the shielding effectiveness by absorption decreased. 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.

EMI SE of the conducting polymer composite films prepared at various concentration of pyrrole was measured and almost same results were obtained. In all of the compositions, the concentration of chitosan and *p*-TS were 0.7% (w/v) and 0.1 molar respectively and applied voltage was 1.2 volt versus SCE. The result is plotted in figure 5.

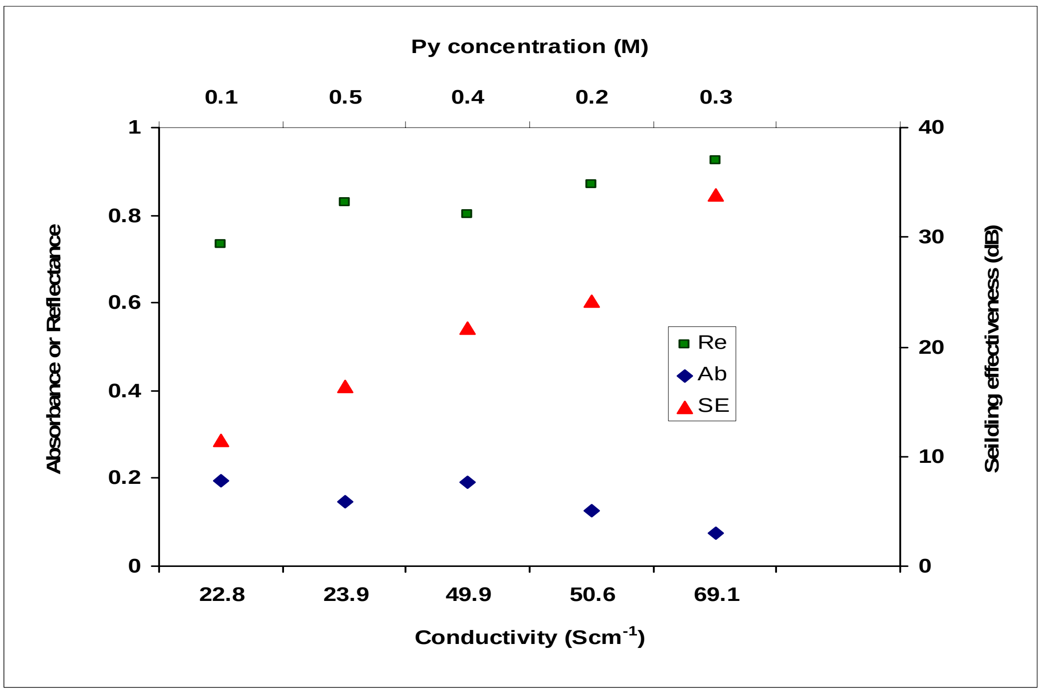

Figure 5: The shielding effectiveness (SE), absorbance, and reflectance of PPy-CHI composite films with various electrical conductivity and different concentration of pyrrole.

As it is shown in figure 5, the EMI SE of the polymer increased with increase in conductivity and the composition of 0.3 molar pyrrole had the highest EMI SE. Reflection increased as a result of increasing in conductivity towards a metallic conductivity. However there is one exception in composition with 0.4 molar Py.

Average values of SE, absorbance, and reflectance over the frequency range are plotted as a function of the conductivity and *p*-TS content in Figure 6.

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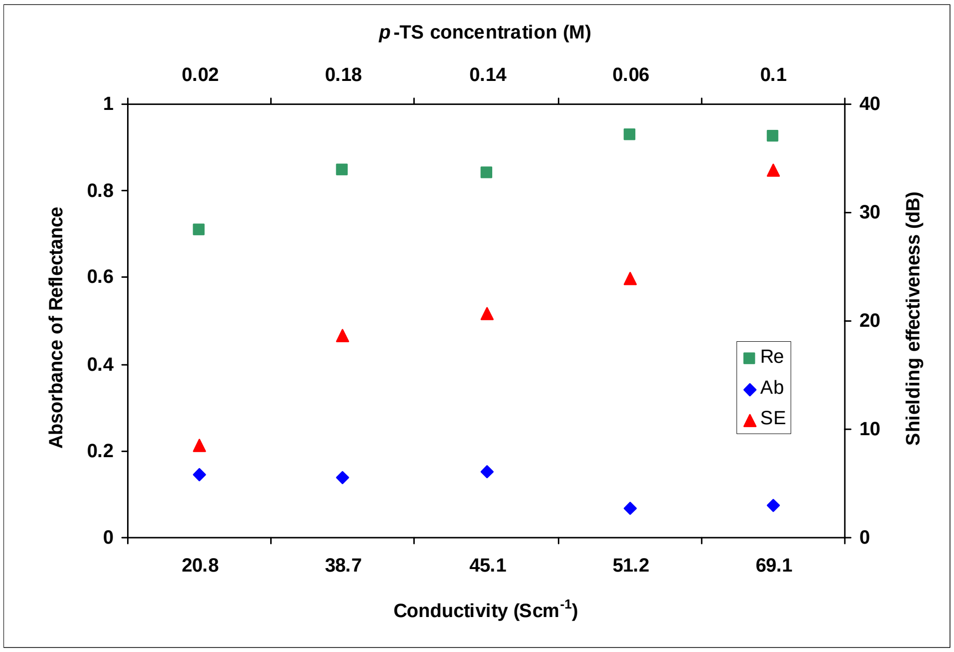

Figure 6: The shielding effectiveness (SE), absorbance and reflectance of PPy-CHI composite films with various electrical conductivity and different concentration of *p*-TS

Like the other experiments SE of the polymer increased with the increase in conductivity but there are some exceptions for the reflection and absorption measurements which it could be as a result of calibration error.

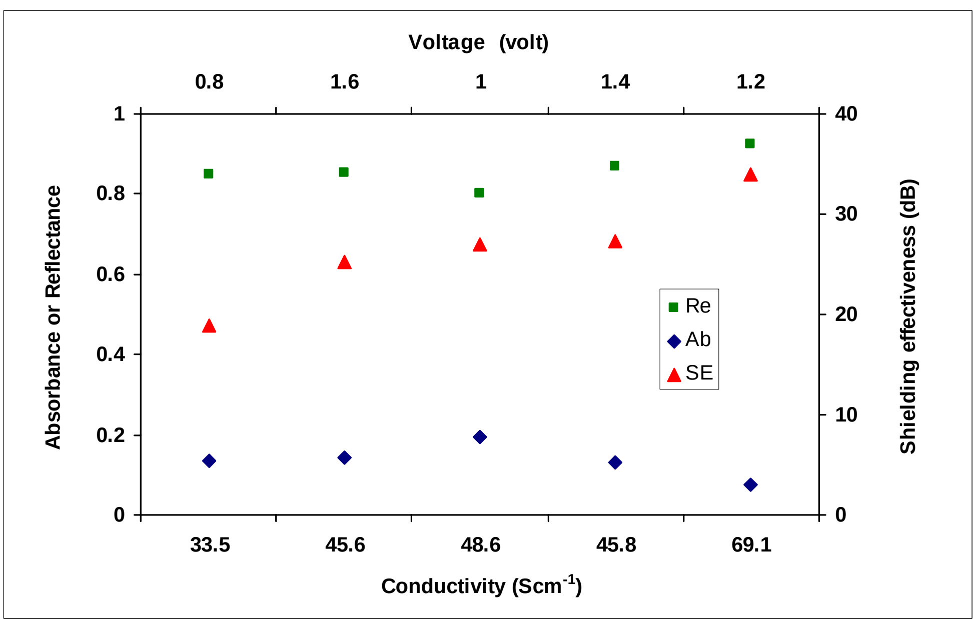

Figure 7: The shielding effectiveness (SE), absorbance, and reflectance of PPy-CHI composite films with various electrical conductivity prepared at different voltages versus SCE.

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The same analysis was done for the conductive polymer composite films prepared at different applied voltages. The concentration of Py, CHI and *p*-TS were 0.3M, 0.7% (w/v) and 0.1 M respectively. The composite films prepared at 0.8 and 1.2 volt were the samples with lowest and highest SE and also conductivity respectively (Figure7).

CONCLUSIONS

Enhanced electrical conductivity and mechanical properties of the composite films are due to the presence of chitosan. Composite film of PPy-CHI compare to PPy without CHI, showed higher conductivity and EMI SE in the frequency rang of 8-12 GHz. This can be considered as an evidence of incorporating of CHI into the polypyrrole structure. The SE and reflection increased with increase in conductivity, while absorption decreased. The decrease of absorption must be due to shallower skin depth of the composite with higher electrical conductivity.

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