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Electromagnetic properties of polypyrrole thin film on copper substrate

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ABSTRACT

Highly adherent and homogeneous polypyrrole thin films were deposited on copper from sodium oxalate solution for different molar concentration. The electromagnetic reflection, absorption, permittivity and conductivity studied in the frequency range 8- 12 GHz is reported. Polypyrrole increases the reflection of copper but decreases the microwave absorption. The absorption is highly dopant concentration dependent. As dopant concentration increases the permittivity and microwave conductivity increases.

Keywords: Polypyrrole; Electromagnetic reflection; Permittivity; Microwave conductivity.

INTRODUCTION

Copper is a metal which is very often used as metallization for high frequency circuit. Copper changes its properties due to ambient effects. The conducting polymer coating on copper may decrease these effects. It is therefore necessary to study the electromagnetic properties of polypyrrole (PPy) when deposited on copper.

In recent years there has been much interest in the development and use of conducting polymers as protective coatings on metals and alloys [1]. Polypyrrole is one of the most promising conducting polymers because of its high conductivity, stability and ease of synthesis. In fact several workers have reported on the protection of corrosion susceptible metals by electrochemically generated PPy [2-5].

Understanding of how the PPy changes the properties of copper is essential, with this in view the electromagnetic studies of PPy thin film on copper substrate is reported. To the author knowledge there are no reference works on electromagnetic properties in the 8-12 GHz range of PPy on copper substrate.

In this paper the deposition of highly adherent polypyrrole film on copper in an aqueous sodium oxalate solution is reported. The electromagnetic (8-12 GHz frequency range) properties such as reflection, absorption, permittivity and conductivity are investigated.

Materials and methods

Pyrrole monomer (Aldrich), Sodium Oxalate ($Na_2 C_2O_4$) (Merck) were used as received, while water was distilled before use. Prior to the electropolymerisation, the substrates were polished to a smooth surface finish using successively finer grades of polish papers, washed with soap solution and distilled water and dried under an air stream and wiped by lint less tissue paper.

The polypyrrole thin film was deposited on the copper substrate using a constant current source in a conventional three electrode cell. A saturated calomel electrode was used as a reference electrode and high density and high surface area graphite rod was used as the counter electrode. The deposition of polypyrrole thin films was carried out using electrolyte solution of 0.3 M pyrrole and 1M and 2M Sodium Oxalate. The current was 8 mA with current density of 3.6 $mA/cm^{2.}$ Adherent black colored polypyrrole thin films were obtained. The thickness of the synthesized polypyrrole thin films was measured by the gravimetric method. The thickness was varied from 2.1µm to 16µm by the change in time of deposition.
The electromagnetic system used for the measurement was the microwave X–band (8 to 12 GHz) waveguide reflectometer [6].

The structure of the polypyrrole film was confirmed from FTIR spectra (Perkin-Elmer-USA) in the range of 450-4000 cm^{-1}. Surface morphology of the polypyrrole films on copper was investigated by scanning electron microscopy (SEM, JEOL-JSM 6360).

RESULTS AND DISCUSSION

The FTIR spectrum of the polypyrrole thin film is shown in figure 1. The FTIR spectra in the range of 450-4000 cm^{-1} shows the presence of major expected peaks of the polypyrrole.

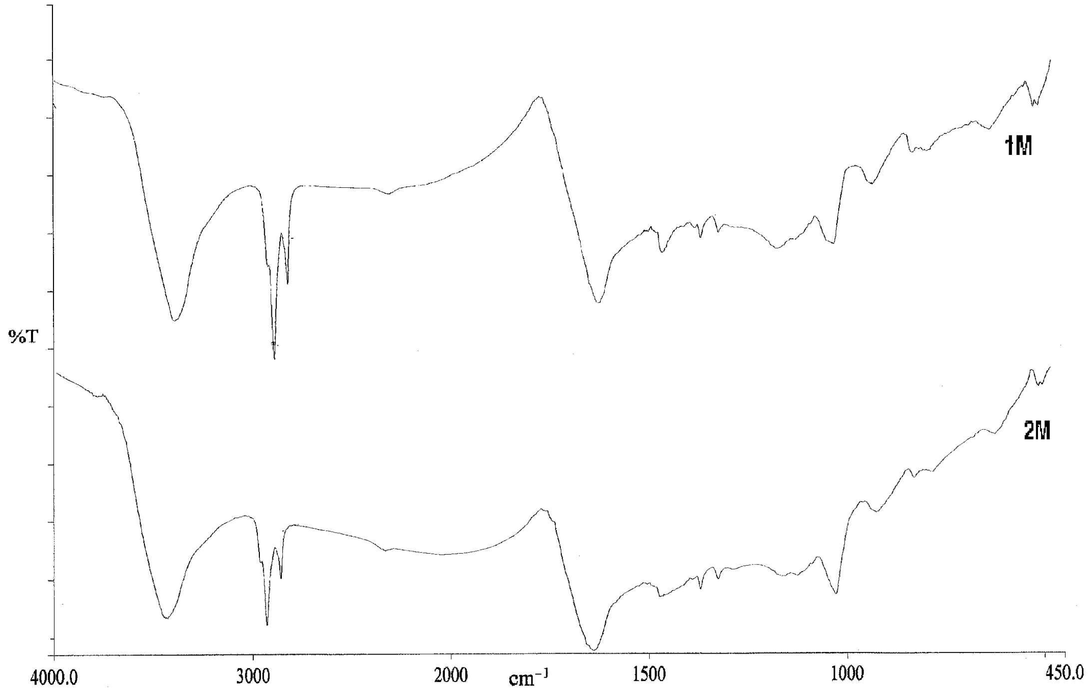

Fig.1. FTIR spectrum of polypyrrole thin film for 1M and 2M Sodium Oxalate concentration

The peak observed at 3444 cm^{-1} has been assigned for N-H stretching for the nitrogen in the pyrrole rings. The peak observed at 2926 cm^{-1} is assigned for aromatic C-H stretching. The conjugated double bonds c = c stretching vibration of pyrrole ring absorbs around 1616 cm^{-1} [7]. This peak was not intense when PPy was deposited on stainless steel [8] but was present when deposited on silver [9].The peak at 1380 cm^{-1} due to C–H bending vibrations obtained when PPy was deposited on silver [9] is suppressed on copper. The peaks obtained at 1234 cm^{-1} for C-N stretching vibration, the peaks at 1024 cm^{-1} and 930.53 cm^{-1} is formed due to doping reaction [10]. The peak at 1024 cm^{-1} is sharper and intense when dopant concentration is increased.

The variations in the surface morphology with respect to variation in the dopant concentration were observed as shown in figure 2(a) and 2(b). From the figure it is seen that as the doping level increases, the grain size of PPy increases. The nature of PPy thin film is like stacked laminar agglomerates. These are different from those obtained on stainless steel and silver [8, 9].It has been reported [11] that the underlying substrate metal produces differences in morphology of the polypyrrole thin film. Due to change in dopant concentration the agglomerates become more compact and lower porosity is obtained.

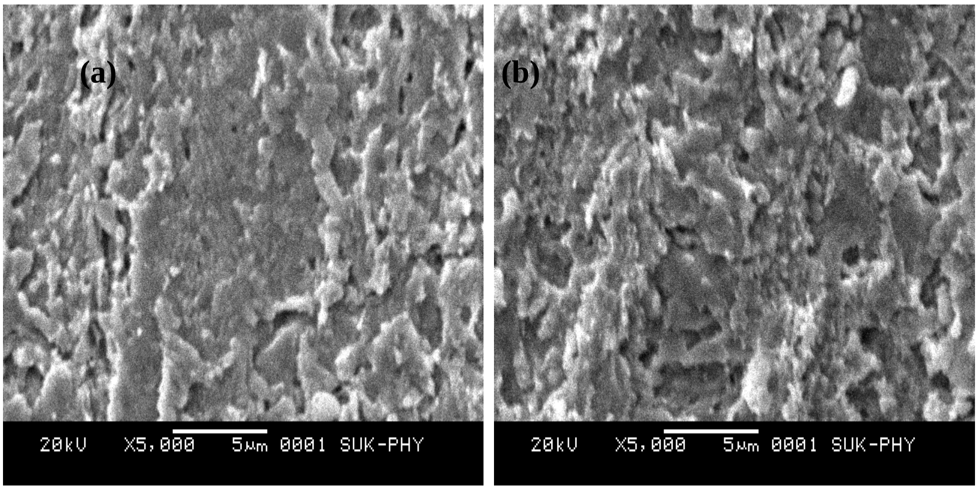

Fig.2: The variations in the surface morphology with respect to variation in the oxalate dopant concentration (a) 1M (b) 2M

The resistance of the film was measured by using two probe method at room temperature. The data of resistance along with calculated DC conductivity is tabulated in table 1.

Table 1: Data of DC conductivity

Thickness (µm)	**Resistivity (ohm/cm)**		**DC conductivity (S/cm)**	
	1M	**2M**	**1M**	**2M**
2.6	9.45	6.6	0.105	0.15
4.8	7.15	2.9	0.140	0.344
8.5	5.4	1.15	0.185	0.869
12.5	3.21	0.857	0.312	1.166

From the table it is seen that as thickness increases, conductivity also increases as expected. As dopant concentration increases DC conductivity increases. DC conductivity varies from 0.15 S/cm and 1.166 S/m. The values are in the range obtained by other workers [12]. The increase in the conductivity due to increase in the thickness might be due to the more compact morphology obtained for these films.

The graph of microwave reflection versus frequency is plotted in figure 3.

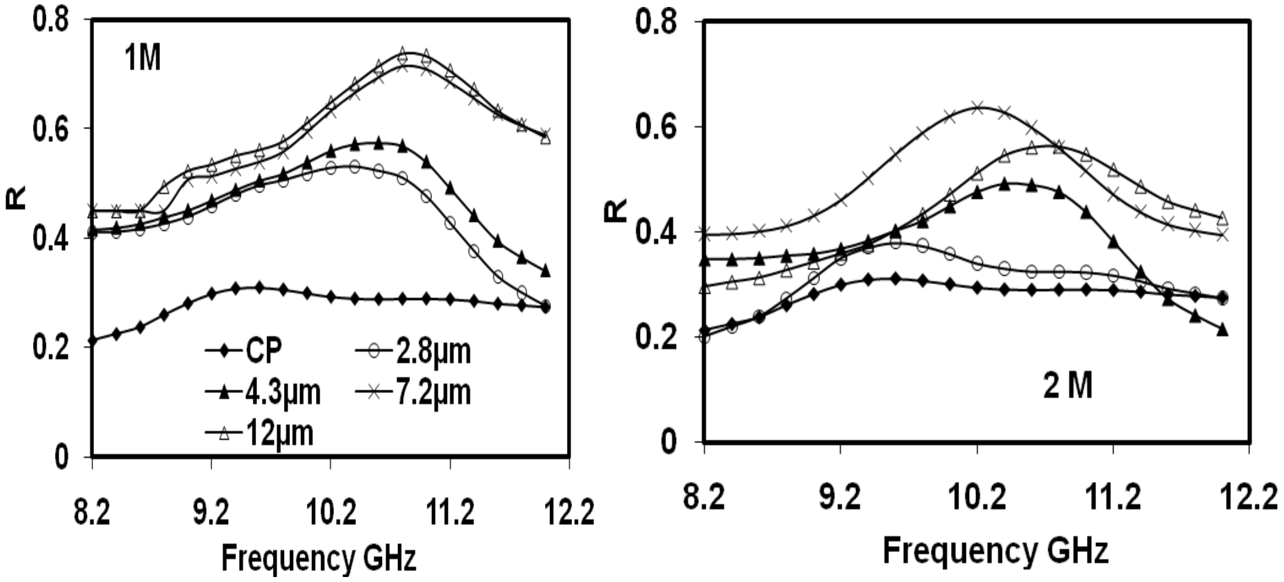

Fig.3: Reflectance of PPy thin films deposited from 1M and 2M Sodium Oxalate on copper. CP- Copper

From the figure 3 it is seen that the reflectance of the PPy thin film decreases with increase in dopant concentration and the reflectance is higher than the copper in the 8 -12 GHz frequency range. The increase is ~ 30-40% at some frequencies and a peaking effect is observed at ~ 11 GHz. The thickness dependent effects are also observed.

The frequency response in the absorption mode is plotted in the figure 4. The absorption plots are complimentary to the reflection. From the figure it is seen that due to polypyrrole thin film the microwave absorption decreases by ~ 30% at ~11 GHz when 1M dopant was used for synthesis and in general the absorption is lower than that of copper in the entire frequency range. The PPy deposited at 2M dopant concentration show higher absorption than copper for larger thickness of the film.

Fig.4: Absorption of Polypyrrole thin films on copper.

In general reflection is the result of interaction between conducting particles in the conducting material (free electron or vacancy) and electromagnetic field. Absorption is caused by the heat loss under the action between electric dipole in the material and the electromagnetic field.

From the position of minima as measured by voltage standing wave ratio slotted section method [13] and reflection coefficient the permittivity was calculated using the following equation [14].

$$\varepsilon' = \left(1 + \frac{\Delta\phi\lambda_0}{360 \times d}\right)^2 \quad \text{and} \quad \varepsilon'' = \left(\frac{\Delta A \lambda_0 \sqrt{\varepsilon'}}{8.686 \times \pi \times d}\right)$$

Where $\Delta\phi$ = difference of the phase shift with and without sample

λ_0 = wavelength of the corresponding frequency

ΔA = difference of the attenuation with and without sample

d = thickness of the sample

The graph of real (ε') and imaginary part (ε") of permittivity versus frequency is shown in figure 5. From the figure it is seen that as frequency increases ε' decreases. The decrease is more for films with lower thickness and for dopant concentration of 1M KNO_3. As thickness increases the dielectric constant decreases for both the dopant concentrations. Due to 1 M KNO_3 concentration ε' decreases from 45.2 to approximately 5.23 and due to 2M KNO_3 the dielectric constant decreases from 57.8 to 4.8 due to increase in thickness.

Fig.5: Dielectric constant and dielectric loss of Polypyrrole thin films on copper

The dielectric loss ε" is almost constant for all the frequencies studied for the polypyrrole deposited in 1M KNO_3 solution, whereas the thinner films show frequency dependent variations when deposited in 2M KNO_3. As thickness increases the dielectric loss also decreases. The ε" decreases from 267 to 23 for the polypyrrole deposited in 1M KNO_3 and decreases from 577 to 42 due to 2 M KNO_3 concentration. Both ε' and ε" increased with increasing dopant concentration. The values obtained by us using the slotted section are in the range obtained by other workers using cavity method [10].

The microwave conductivity of the PPy is shown in figure 6. The conductivity can be related to the imaginary part of the dielectric constant [15]

$$\sigma = \omega\varepsilon'' = 2\pi f \varepsilon_0 \varepsilon''$$

Where f = frequency, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, ε"= imaginary part of dielectric constant

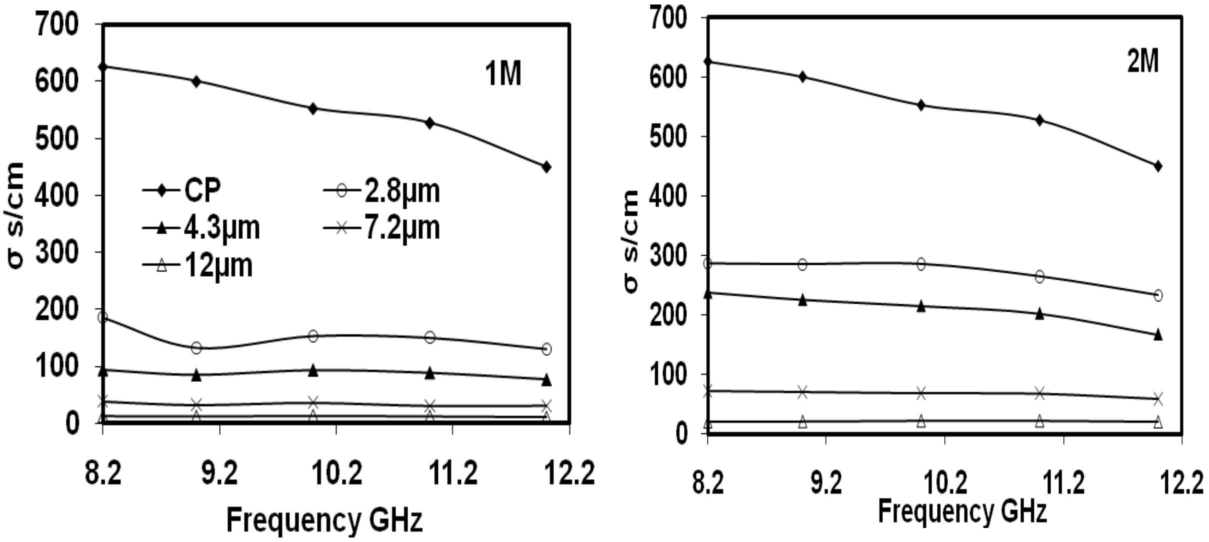

Fig.6: Microwave conductivity of Polypyrrole thin films.

From the figure it is seen that microwave conductivity (σ_{mw}) decreases as thickness increases and varies between 286 S/cm to 10 S/cm. Higher the dopant concentration larger the microwave conductivity obtained.

Microwave conductivity has been found to be much larger than dc conductivity for the insulating base, but for more conducting salts microwave conductivity approaches the dc conductivity. This may be due to low protonation. For higher protonation levels, microwave conductivity approaches the DC conductivity at room temperature [16]. The higher conductivity indicates more mobile charges that can interact with the electromagnetic fields in the radiation. Impedance of the material with high conductivity is very small relative to air, so that the skin depth is very small and hence larger reflection is obtained. Also larger reflection is obtained for materials with high dielectric constant. The electromagnetic absorption depends on the level of the conductivity and the permittivity of the materials and their variation with frequency [17]. Efforts are being made to achieve properties similar to copper so as to replace copper metallization by polypyrrole for microwave applications.

CONCLUSION

The electromagnetic reflection and absorption data shows the PPY film increases the microwave reflectance of copper but makes the copper less absorbing. The microwave conductivity is larger than the DC conductivity by many orders of magnitude. The films with lower thickness gives lower reflectance, higher ε', ε" and conductivity. The corrosion protection application of polypyrrole thin film is well known. For microwave antenna application where the reflectance, conductivity and shielding effectiveness of the antenna are important the coating of polypyrrole thin film can be useful. As seen the reflectance of PPy is higher than that of copper in the X band, they enhance the gain and protect copper of reflector antennas.

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