Chapter 8

APPLICATION STUDY:
MICROWAVE ABSORPTION, REFLECTION, EMI SHIELDING AND MECHANICAL PROPERTIES OF PANI-PU COMPOSITE

Abstract: In order to allow the coexistence of all electronic components without harmful electromagnetic interferences, it is necessary to develop new shielding and absorbing materials with high performance and a large operating frequency band. Conducting polymer composites were found suitable for EMI shielding and for the dissipation of electrostatic charge. In the present study PANI-PU composite was considered for these applications. The microwave absorption, microwave reflection and EMI shielding properties of PANI-PU composite are evaluated both at S band and X band frequencies. The material is found to have good microwave absorption and is a potential candidate for EMI shielding applications. The mechanical properties of the composite film are found to be satisfactory for normal service conditions. The composite shows change in conductivity with load and hence can be applied in load and pressure sensing applications.

The continuous growth of the telecommunication market has led to the emergence of a huge number of Radio Frequency (RF) systems. In order to allow the coexistence of all of those various instruments without harmful electromagnetic interferences, it is necessary to develop new shielding and absorbing materials with high performance and a large operating frequency band. Conducting polymers are
characterized by attractive features like high anticorrosion property, controlled conductivity, high temperature resistance, low cost and ease of bulk preparation. These properties make conducting polymers as good shielding materials for electromagnetic interference (EMI) [1, 2]. EMI can be defined as spurious voltages and currents induced in electronic circuitry by external sources. In recent years, electromagnetic pollution has received wide attention because of the malfunctioning of the electronic equipments from the radiations generated from the source or those emanating from other electronic equipments. So far conducting composites were made by adding metallic fillers, C-black or metallic powders. Because of certain disadvantages like labour intensity, relatively high cost and time consumption, and the galvanic corrosion observed in metal composites, conducting polymer composites were found suitable for EMI shielding and for the dissipation of electrostatic charge.

Great interest has been focused on polyaniline (PANI), within the conducting polymers field due to its important characteristics, such as, its easy synthesis route, low cost, high-yield, high levels of electrical conductivity, excellent chemical stability etc. Moreover, these properties can be well controlled and are reproducible. The microwave properties of PANI are considerably influenced by their structural parameters, which are dependent on the synthesis routes, doping methods and dopant natures [3]. Because of the poor mechanical properties of conducting polymers it is necessary to blend them with a matrix, usually based on polymeric systems. One of the methods to process PANI, without altering the structure of the polymer, is by blending it with conventional polymers. These blends may combine the desired properties of the two components, the electrical conductivity of PANI with the physical and mechanical properties of the polymeric matrix [4, 5]. Poly aniline and polypyrrole with different proportion of PVC were
prepared and studied at the S-band microwave frequencies. These materials were found to exhibit good EMI shielding behaviour [1].

The research and development of RAM (Radar absorbing Materials) has attracted considerable interests in recent years to eliminate or reduce spurious electromagnetic radiations present in the environment, caused as a consequence of technological advances in telecommunication area and the proliferation of wide variety artefacts that employ high frequencies [6]. The first reported use of RAM was made during World War II, when the Germans applied a mixture of polymeric foam and carbon black on the submarine periscopes to avoid radar detection [7].

The purpose of the widely broadcasted ‘Stealth technology’ is the reduction of the aircraft RCS (Radar Cross Section). The Radar Cross Section is a measure of reflective behaviour of a target. It is defined as $4\pi$ times the ratio of the scattered power per solid angle unit in a specific direction to the power, per unit area in a incident wave plane on the scatterer from a specified direction. More precisely, it is the limit of that ratio as the distance from scatterer to the point where the scattered power is measured approaches infinity [8].

It is absolutely essential for the preparation of RAM, based upon conducting polymers, that the material allows electrical conductivity variation [9]. Therefore, this parameter determines the characteristics of radiation absorption of the conducting polymer, supporting the exchange of incident electromagnetic energy on material by thermal energy. The control of the electrical conductivity is directly related to the efficiency of the processed absorber under the influence of polymer chain size, doping level, dopant type and the conducting polymer syntheses methods [9]. It is well-known that these parameters can cause changes in molecular structures, modifying consequently the electromagnetic properties of radar
absorbing material. These unique characteristics of the conducting polymers make them a set of modulating absorbing centers, allowing to make some changes on final characteristics of the radar absorbing material [10]. Therefore, the domain of the radiation absorbing centers ensures the acquisition of broadband or resonant absorbing materials with previously established absorption frequency range. Indeed, the wide conductivity range and the differences in molecular structures due to the use of different dopants, helps to achieve very efficient absorbers [11].

In general, considering the use of absorbing center in X-band, the following operational requirements are needed, attenuation of the incident radiation at a minimum of 50% (-3 dB), in the operational broadband frequency range, minimum attenuation of 99% (-20dB) in narrow band range (resonant absorber) reduced thickness (smaller than 3mm) and low density [9, 12].

PANI-PU composite was found to have good microwave absorption and EMI shielding. In this study, the microwave absorption, microwave reflection and EMI shielding properties of PANI-PU composite is proposed to be investigated at a larger span of frequencies both at S band and X band. For any product moderate mechanical properties are essential and hence the mechanical properties are also proposed to be studied.

When FeCl$_3$ was used as the oxidant in preparing the composites, the films tend to adsorb moisture on long storage. This may be due to the hygroscopic nature of FeCl$_3$. To overcome this problem benzoyl peroxide is proposed to be used as the oxidant in the following studies.
8.1 EXPERIMENTAL METHODS

PANI-PU composite was prepared with a FeCl₃: Monomer ratio of 2.5. Aniline was added to PU solution in THF to get a 10% 1:1 PU-aniline mixture. 0.5 M benzoyl peroxide was added to the solution and the reaction was carried out for 24 hrs. Doping of composites was done by adding camphor sulfonic acid (CSA) to the composite solution in the ratio aniline: CSA (1: 0.5).

8.1.1 Absorption coefficient, reflection coefficient and EMI shielding

From the measurement of S-parameters, absorption coefficient and the shielding efficiency of the material could be calculated. The sample sheet was kept between two coaxial to wave guide adapters and tightened. Using the Agilent E8362B PNA series network analyzer, the S-parameters, ‘S₁₁’ and ‘S₂₁’ were measured. Reflection coefficient ‘R’ and transmission coefficient ‘T’ are given as $R = |S_{11}|^2$ and $T = |S_{21}|^2$. The absorption coefficient ‘A’ can be obtained from the simple relation $A + R + T = 1$. The EMI shielding efficiency ‘SE’ is defined (Equation 1) as the ratio of the power of the incident wave ‘$P_I$’ to that of the transmitted wave ‘$P_T$’.

$$SE = 10 \log \left( \frac{P_I}{P_T} \right) \text{dB}$$ (1)

8.1.2 Mechanical properties

The mechanical properties of the composite were evaluated in Shimadzu Autograph AG-1 series UTM of 10 kN load capacity. Dumbbell specimens were
cut from cast films from different area and they were subjected to tensile tests at a rate of 15 mm/sec.

8.1.3 Load sensitivity

The conductivity of the samples at various loads were carried out by a two-probe technique recorded by a Keithley 2400 Sourcemeter and a Keithley 2182 Nanovoltmeter. Conductivity measurements were done using cast films. The specific resistivity was calculated as:

\[ \rho = \frac{R \times A}{t} \]

where, \( \rho \) is the resistivity, \( R \) is the resistance measured, \( A \) is the area of the electrode used and \( t \) is the thickness of the sample and,

\[ \sigma = \frac{1}{\rho} \]

where, \( \sigma \) is the conductivity of the material. The conductivity was measured at various standard loads.

8.2 RESULTS AND DISCUSSION

In this section the microwave absorption, microwave reflection, EMI shielding and mechanical properties of PANI-PU composite are analyzed.

8.2.1 EMI shielding

Variation of EMI shielding of the PANI-PU composite for different thickness at S band frequencies is given in Figure 8.1.
Figure 8.1 Variation of EMI shielding (SE) of the PANI-PU composite for different thickness at S band frequencies.

The higher the SE value in decibel (dB), lesser the energy passing through the sample. All measured SE is the combination of the electro magnetic (EM) radiation, i.e. reflection from the material’s surface, absorption of the EM energy and multiple internal reflections of the EM radiation [13].

From the Figure 8.1 it can be seen that shielding efficiency increases with the thickness of the sample but the trend remains the same. Maximum shielding efficiency in S band frequencies occurs at 2.23 GHz. The shielding efficiency for a thickness of 0.62 mm is 6.3 dB and that at 1.26 mm is 10.2 dB. So it can be inferred that this material is ideal for shielding at 2.23 GHz.
Variation of EMI shielding of the PANI-PU composite for different thickness at X band frequencies is given in Figure 8.2

![Graph showing variation of EMI shielding (SE) of the PANI-PU composite for different thickness at X band frequencies.](image)

Figure 8.2 Variation of EMI shielding (SE) of the PANI-PU composite for different thickness at X band frequencies.

From the figure it can be seen that shielding efficiency increases with the thickness of the sample but the trend remains the same. Maximum shielding efficiency in X band frequencies occurs at 8.82 GHz. The shielding efficiency for a thickness of 0.62 mm is 18.2 dB, at 1.26 mm is 20 dB and that at 1.9 mm is 26.7 dB. The next
peak occurs at 10.18 GHz. The shielding efficiency for a thickness of 0.62 mm is
10.3 dB, at 1.26 mm is 13 dB and that at 1.9 mm is 15.5 dB. So it can be inferred
that this material is ideal for shielding at 8.82 GHz.

Minimal reflection of the microwave power or matching condition occurs when the
sample's thickness, 't' of the absorber approximates to a quarter of the propagating
wavelength multiplied by an odd number, that is \( t = n\lambda / 4 \) (n=1, 3, 5, 7, 9, ...),
where n=1 corresponds to the first dip at low frequency. The propagating
wavelength in the material (\( \lambda \)) is given by:

\[
\lambda = \lambda_0 / \left( |\mu_r^*| / |\varepsilon_r^*| \right)^{1/2}
\]

(2)

where, \( \lambda_0 \) is the free space wavelength and \( |\mu_r^*| \) and \( |\varepsilon_r^*| \) are the moduli of \( \mu_r^* \)
and \( \varepsilon_r^* \) respectively. The matching condition can be explained by the cancellation
of the incident and reflected waves at the surface of the absorber [14]. Similar
peaks and dips have been reported by Phang et al. for polymers. The minimum
reflection loss or the dip is due to the minimal reflection or maximal absorption of
the microwave power for the particular thickness of the sample. The position and
intensity of dip are sensitive to the thickness [15].

8.2.2 Absorption coefficient

Variation of absorption coefficient of the PANI-PU composite for different
thickness at S band frequencies is given in Figure 8.3
Figure 8.3 Variation of absorption coefficient of the PANI-PU composite for different thickness at S band frequencies.

From the figure it can be seen that absorption coefficient increases with the thickness of the sample but the trend remains the same. Variation of absorption coefficient of the PANI-PU composite for different thickness at X band frequencies is given in Figure 8.4.
Figure 8.4 Variation of absorption coefficient of the PANI-PU composite for different thickness at X band frequencies.

From the figure it can be seen that absorption coefficient increases with the thickness of the sample but the trend remains the same. The peak tends to straighten as the thickness increases which show that after a certain thickness the frequency dependency may not exist.

The behaviour of electromagnetic absorption will critically depend on dielectric and magnetic properties of the materials that are represented by the complex permittivity and complex permeability [16]. PANI-PU composite is organic in nature without any addition of magnetic fillers like carbonyl iron and ferrite, thus the microwave absorbing property of is solely attributed to the dielectric constant, $\varepsilon'$ of the composite.
The frequency dependence of the microwave properties can be attributed to various relaxation processes. At very low frequencies Debye type of relaxation processes occur. Another possibility is the interfacial polarization relaxation effects and dipolar reorientation processes in polymers [17]. The dispersion of conductive regions in a less or non conducting medium is known to lead to Maxwell–Wagner–Sillars (MWS) effect [17-19]. The exact mechanisms can be known from the calculation of relaxation times, activation energies and analysis of dielectric relaxation spectra of the composite. The nature of the polymer matrix is found to influence the relaxations by frequency shift, change in relaxation strength and activation energy [19].

8.2.3 Reflection coefficient

The variation of reflection coefficient of the PANI-PU composite for different thickness at S band frequencies is given in Figure 8.5

The reflection behaviour of microwaves from the samples is seen to be frequency dependent. As the thickness increases the reflection increases but the trend remains the same. Phang et al. have reported a sharp increase in reflection of microwaves from PDPV samples above 2 mm thickness below 5 GHz [15].

The variation of reflection coefficient of the PANI-PU composite for different thickness at X band frequencies is given in Figure 8.6.
Figure 8.5 Variation of reflection coefficient of the PANI-PU composite for different thickness at S band frequencies.

Figure 8.6 Variation of reflection coefficient of the PANI-PU composite for different thickness at X band frequencies.
Comparing Figure 8.5 and 8.6 we can see that the reflection is comparatively low at X band compared to that at S band. The variations of reflection coefficient with frequency at S band and X band show similar behaviour. Reflection seems to be very frequency specific. As the thickness increases the reflection increases but the trend is maintained up to a thickness of 2 mm.

Minimal reflection of the microwave power or matching condition occurs when the sample’s thickness, \( t \) of the absorber approximates a quarter of the propagating wavelength multiplied by an odd number, that is \( t = \frac{n\lambda}{4} \) \((n=1, 3, 5, 7, 9, \ldots)\), where \( n=1 \) corresponds to the first dip at low frequency. The propagating wavelength in the material \( (\lambda) \) is given by equation (2).

The matching condition can be explained by the cancellation of the incident and reflected waves at the surface of the absorber [14]. Similar peaks and dips have been reported by Phang et al. for polymers [15].

**8.2.4 Mechanical properties**

The samples were subjected to tensile tests in Shimadzu Autograph AG-1 series UTM and the modulus and elongation values for the PANI-PU composite is given below.

Modulus = 3 N/mm\(^2\)
Elongation at break = 650%

The mechanical properties of the composite are found to be satisfactory for normal service conditions to be use as EMI shielding or microwave absorbers.
8.2.5 Load sensitivity

The variation of conductivity for the PANI-PU and PANI-PVC composite with load is given in Figure 8.7.

![Figure 8.7 Variation of conductivity for the PANI-PU and PANI-PVC composite with load](image)

From the figure it can be seen that the conductivity varies with load for both the composites and hence can find application in load and pressure sensors.
8.3 CONCLUSIONS

The microwave absorption, microwave reflection, EMI shielding and mechanical properties of PANI-PU composite were analyzed. The shielding efficiency of the composite increases with the thickness of the sample and this material is ideal for shielding at 2.23 GHz and at 8.82 GHz. The variations of reflection coefficient with frequency at S band and X band show similar behaviour. Reflection of microwaves from the PANI-PU films is very frequency specific. As the thickness increases the reflection increases. Minimal reflection of the microwave power or matching condition occurs when the sample’s length approximates a quarter of the propagating wavelength multiplied by an odd number. This is interpreted as due to the cancellation of the incident and reflected waves at the surface of the absorber. The position, intensity and number of dips are dependent on the thickness of the sample [14, 15].

The material is found to show good microwave absorption and EMI shielding characteristics. The mechanical properties are found to be satisfactory for normal service conditions. The conductivity of the PANI-PU and PVC-PANI composites vary with load and hence can find application in load and pressure sensors.
8.4 REFERENCES


