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# Microwave properties of electropolymerised polyaniline thin films on stainless steel

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**ABSTRACT**

*This paper reports the X-Band (8-12GHz) and Ku-Band (13-18GHz) microwave transmittance and reflectance of polyanline thin films electropolymerised on stainless steel substrate. The waveguide reflectometer method has been used for the microwave studies. The polyanline thin film changes the transmission and reflection properties of SS substrate. The effect of moisture on polyaniline thin films has been also reported. The larger dispersion is observed after moisture exposure. The thickness dependent properties are not very prominent. The frequency and current during deposition changes are observed.*

**Key words:** Polyaniline Thin films, Transmission, Reflection, shielding effect.

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## INTRODUCTION

Conducting polymers are such as polyaniline and polypyrrole have generated much interest in scientific research as suitable candidates for the replacement of metals. Among the various conducting polymers, polyaniline (PANI) has a special representation due to easy synthesis, environmental stability, low cost and high conductivity [1-8]. Stainless steel (SS) is a very popular material for fabrication of dish antenna used in radio astronomy, radars, remote sensing etc. Though SS is a good material for fabrication of antennas, it absorbs microwave so there is a need to modify surface properties of stainless steel. This may done using conducting polymers. PANI is one of the most versatile conducting polymers with interesting electrical, electrochemical, optical characteristics along the excellent environmental stability and its raw material can be obtained easily [9-13]. The microstructure of the conducting PANI can vary with the conditions of synthesis. Electropolymerisation is a simple method for deposition of nano structured PANI thin films. The structure can be granular [14-15], fibular [16-17] or flasky [18].

In this work, for the microwave study of PANI thin films waveguide reflectometer technique has been used. The thin films deposited by Electropolymerisation method on SS substrate. The change in transmittance ΔT and the change in reflectance ΔR of PANI thin films are reported. The effect of moisture on PANI thin films is also reported. The shielding effectiveness of PANI thin films are also reported.

## MATERIALS AND METHODS

The PANI thin films were deposited by Electropolymerisation method [19]. Prior to the Electropolymerisation, the substrate were polished to a smooth surface finish using successively finer grades of polish papers, washed with a soap solution and distilled water, dried under an air stream and wiped by lint less tissue paper because it affects morphology, smoothness, uniformity and adhesion of the material. The PANI thin films were deposited on the SS substrate at constant current 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 electrolyte solution contained 1M aniline and 2M $H_2SO_4$. Adherent dark yellowish green (shiny matt) thin films were obtained. During the deposition of polyaniline thin films, the effect of the deposition parameters on the thickness of the films was investigated. In one set, the PANI films SA,SB,SC and SD of same thickness 3µm were obtained with varying a current and time deposition and in the other set, the PANI films SS-A, SS-B, SS-C and SS-D are different thicknesses 2.5, 5, 10 and 15µm respectively were obtained with keeping same current (3mA) and varying deposition time. The size of substrate was 5cm×1.1cm.

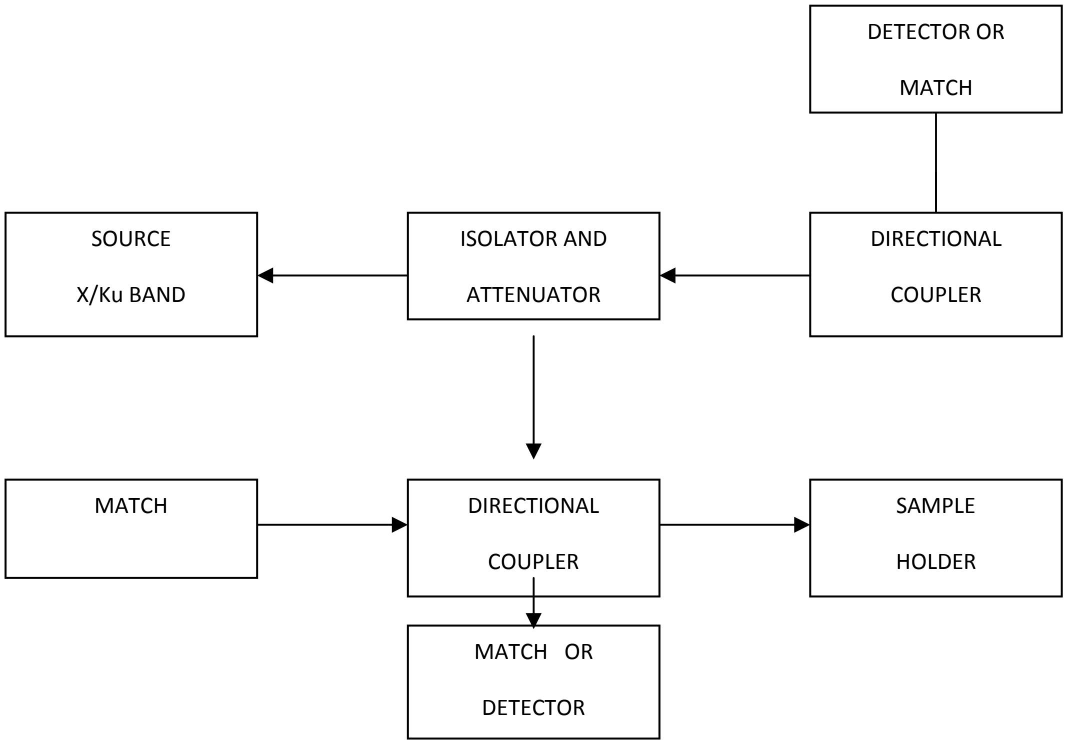



**Fig. 1. Schematic microwave measurement set up.**

The microwave system used for the measurement was the X-Band (8-12GHz) and Ku-Band (13-18GHz) waveguide reflectometer consisting of gun source, isolator, attenuator, directional coupler, component under test and detector. Fig. 1 shows the schematic diagram of the microwave measurement setup. The structure of PANI thin films was confirmed from FTIR spectra (Perkin- Elmer, USA) in the range of 450-4000 $cm^{-1}$. The visible absorption spectra of polyaniline were recorded with UV-VIS-NIR 300, HITACHI, JAPAN spectrometer. The SEM surface morphology of polyaniline thin films was imagined by [SEM, JEOL- JSM 6360] scanning electron microscopy. The microwave measurement in change in transmittance and change in reflectance before and after moisture of a sample was calculated by reflectometer technique.

## RESULTS AND DISCUSSION

### 3.1 Film Thickness:

The thickness of the synthesized polyaniline thin films was measured by gravimetric method. The average film thickness'd' in µm is given by, $d = \frac{W}{A\ \rho}$ Where, W = Weight difference in gm, A = Area of the film, ρ = density of the film in $gm/cm^3$

The thickness of the polyaniline thin films varied from 2.5 to 15µm.

### 3.2 D C Conductivity:

Table 1. shows the data of thickness resistivity along with calculated D C conductivity. The resistance of film measured by using two probe methods at room temperature. From the table it is seen that as thickness of PANI thin films increases, the conductivity is also increases.

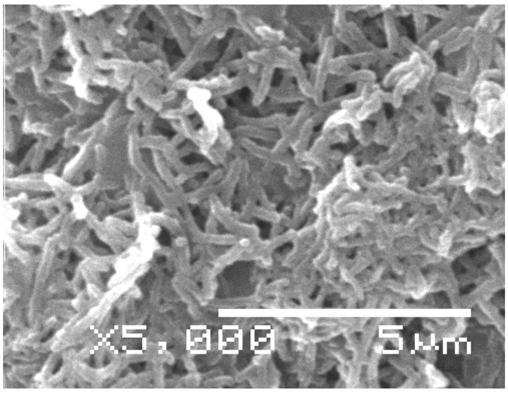
**Table1. Thickness, Resistivity and conductivity of PANI thin films on stainless steel.**

| Thickness of film (μm) | Resistivity (KΩ-cm) | Conductivity $10^{-3}$ (S/cm) |
|---|---|---|
| 2.5 | 10.766 | 0.0928 |
| 5 | 4.021 | 0.2486 |
| 10 | 1.430 | 0.6993 |
| 15 | 0.568 | 1.7583 |

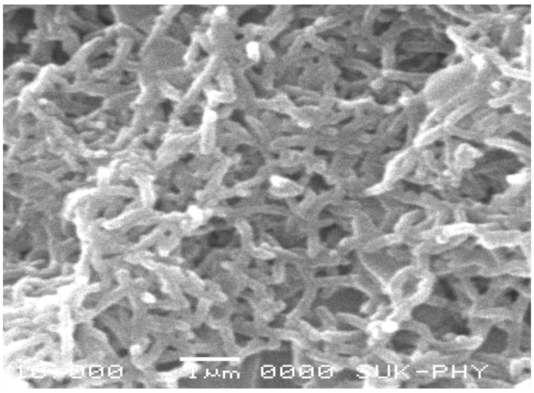
The D C conductivity varies from $0.092 \times 10^{-3}$ S/cm to $1.758 \times 10^{-3}$S/cm. The conductivity of PANI thin films are in the range reported by others[20-22].

**3.3 Morphology using SEM:**

The variations in the surface morphology due to variation in the dopant concentration of polyaniline on SS substrate prepared in 1M and 2M $H_2SO_4$ with 1M aniline was observed as shown in figures 2(a) and 2(b). The striking feature of these micrographs is the presence of fibrils throughout the polymer surface. From the figure it is seen that as the doping level increases, the fibrous nature of the films increases with higher porosity. The fibers are 40 nm to 55nm in size. The morphology of fibrils is highly homogeneous shown in fig. 2(b). Such fibril like structure has been reported. [23].




a) **1M $H_2SO_4$**




b) **2M $H_2SO_4$**

**Fig 2. The variation in the surface morphology with respect to variation in acid concentration**

**3.4 Optical Absorption Studies**:

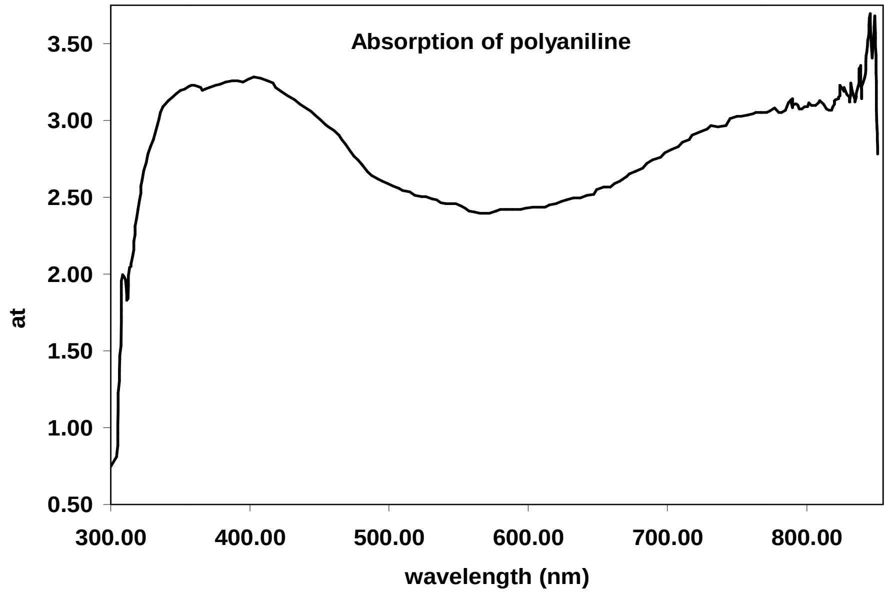



**Fig 3. The optical absorption of polyaniline thin film prepared in 2M $H_2SO_4$.**

The visible absorption spectra of PANI were recorded with UV-VIS-NIR 300, HITACHI, JAPAN spectrometer. The absorption peaks near 400nm and over 800 nm is responsible for green color emeraldine form of PANI films which is conducting in nature are present and is shown in fig.3. The polyaniline thin film on SS in $H_2SO_4$ acid had a band gap of ~ 2.4 eV. [24] Reports the band gap of pure polyaniline is 3.04 eV. The absorption peaks at 1.5 and α ~ 3.3 eV has been reported [25] for bulk polyaniline obtained from HCl..

**3.5 Microwave measurements:**

In microwave measurement, all the data has been plotted as difference in transmittance ΔT and difference in reflectance ΔR between polyaniline thin film and substrate. The change in transmittance ΔT and the change in reflectance ΔR as a function of frequency for polyaniline thin films synthesized under current variation and thickness variation conditions in X-Band are shown in fig.4 (a). From the fig. it is seen that the change in transmittance due to PANI thin films synthesized under current variation condition from bare steel substrate is ~ 10% and due to PANI thin films synthesized under thickness variation condition is 10 TO 20% increases in the frequency range 8.5 to 10.5GHz. Also it is seen that the change in transmittance increases with increases in thickness.

In case of change in reflectance in X-Band, thickness dependent and current dependent changes are not very prominent for all the films but frequency dependent increase and decrease of reflectance is obtained for frequencies below 9 GHz and above 10.5 GHz. The variation is up to 20% is obtained. At 9.2 GHz a sharp increase up to ~ 70% is obtained. This type of sudden change is not observed in case of transmittance.

The fig.4 (b) shows the change in transmittance ΔT and the change in reflectance ΔR as a function of frequency for polyaniline thin films synthesized under current variation and thickness variation conditions in Ku –Band. From the fig., in general the change in transmittance shows increasing trend. There is not much change due to current during deposition or due to thickness of the film. The change in reflectance shows variation in

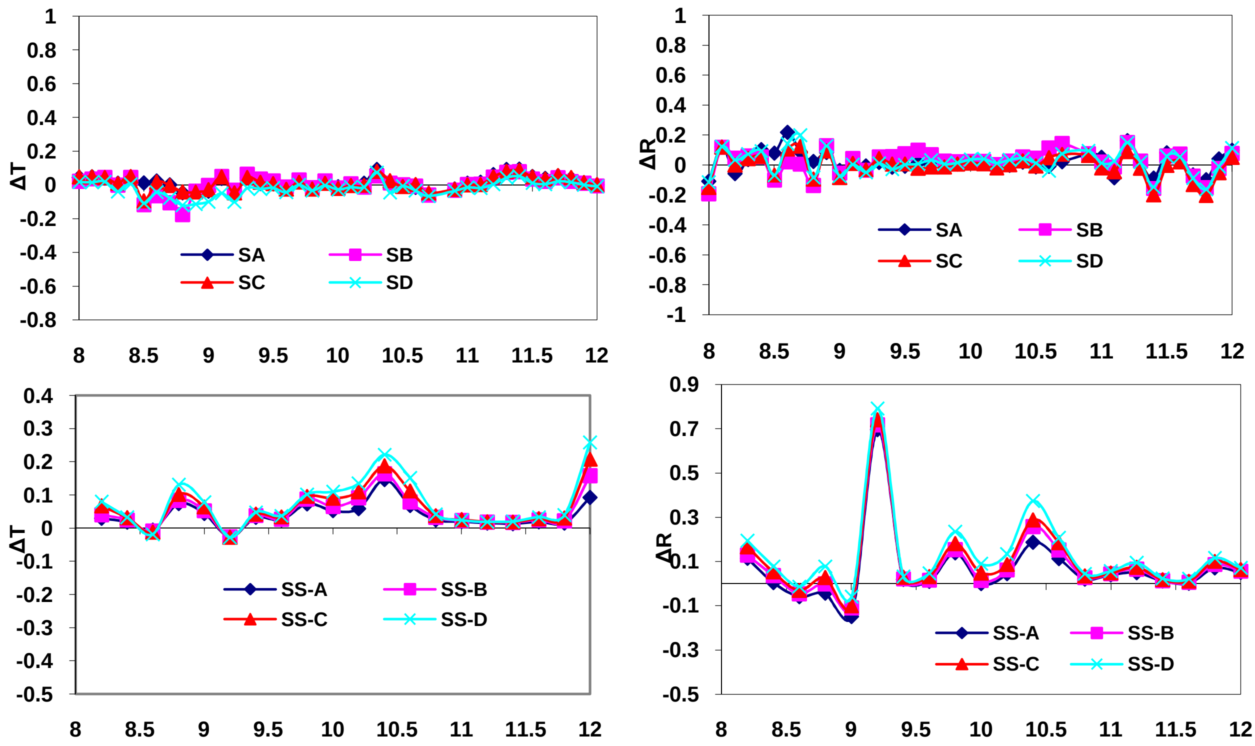



**Fig 4. (a) Change in transmittance and reflectance as a function of frequency in X-band.**

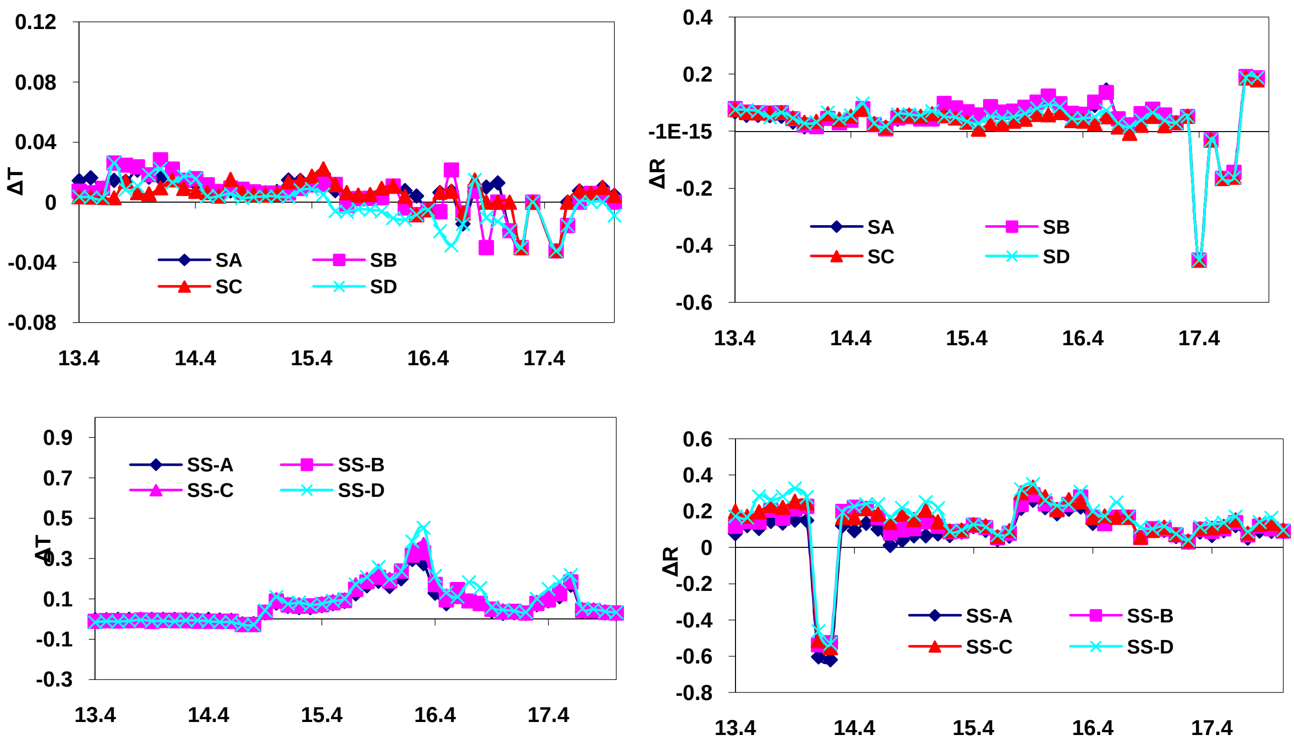



**Fig 4. (b) Change in transmittance and reflectance as a function of frequency in Ku-band**.

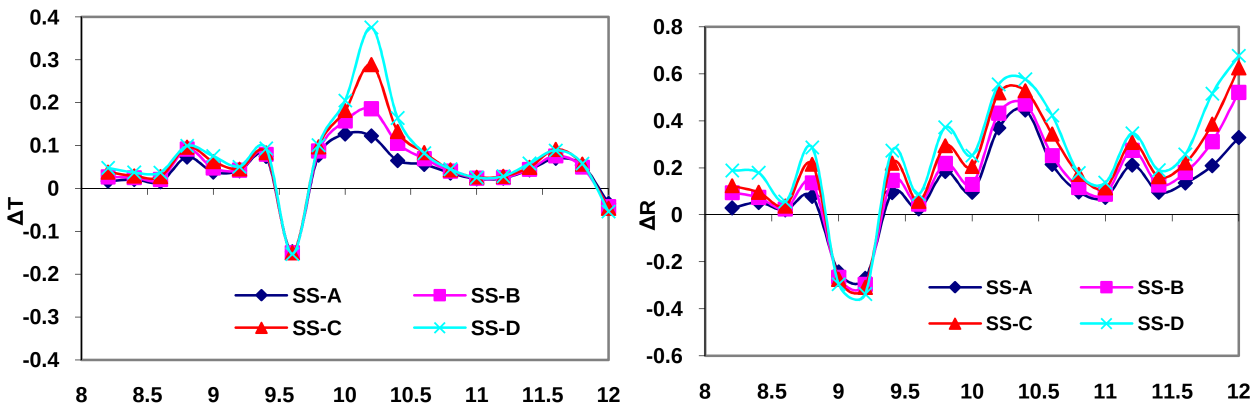



**Fig. 5 (a) Change in transmittance and reflectance as a function of frequency after moisture content in X-band.**

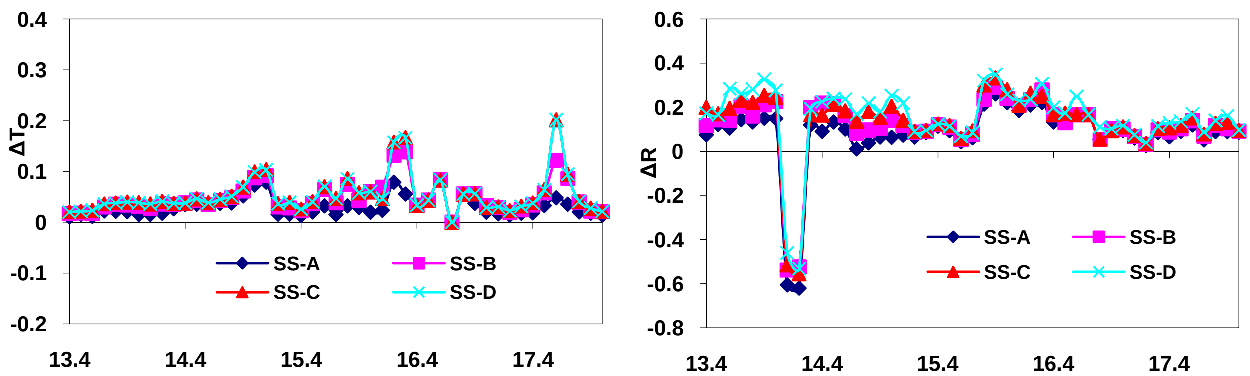



**Fig. 5 (b) Change in transmittance and reflectance as a function of frequency after moisture content in Ku-band.**

reflectance is between 1% to ~15% in the frequency range 13.4 to 17 GHz for the films and beyond 17GHz frequency dependent changes observed.

### 3.6 Microwave measurements due to moisture.

The change in transmittance and change in reflectance of 95% moisturized polyaniline thin films as a function of frequency in X-band and in Ku –Band is as shown in figure 5(a) &5(b). In X-Band, compare to fig. 5 (a) & 4(a), the shape of the curve is different due to moisturized PANI thin films. A sharp decrease in transmittance is obtained at 9.6 GHz and 12 GHz. At 10.3GHz thickness dependent changes shows increase in transmittance with increase in thickness. The shape of change in reflectance curves is almost similar except between 9-9.5 GHz. In this frequency range a sharp decrease in reflectance is observed. At other frequencies beyond 9.5 GHz substantial increase in reflectance is obtained. Thicker films show larger changes than thinner films.

From fig. 5(b) & 4(b), due to moisture the reflectance of PANI increases (+ve ΔR). Thickness dependent changes are not prominent. The sharp decrease observed in figure 5 (b) at 15.2 GHz for PANI on stainless steel has shifted to 14.1 – 14.2 GHz due to moisture exposure. PANI thin films show larger changes in reflectance for frequencies greater than 15.5 GHz.

### 3.7 Shielding Effectiveness:

Electromagnetic shielding effectiveness is described as the attenuation of electromagnetic radiation by reflection or absorption in a material. The microwave shielding effectiveness of PANI thin films have been calculated from transmission coefficient of the sample.

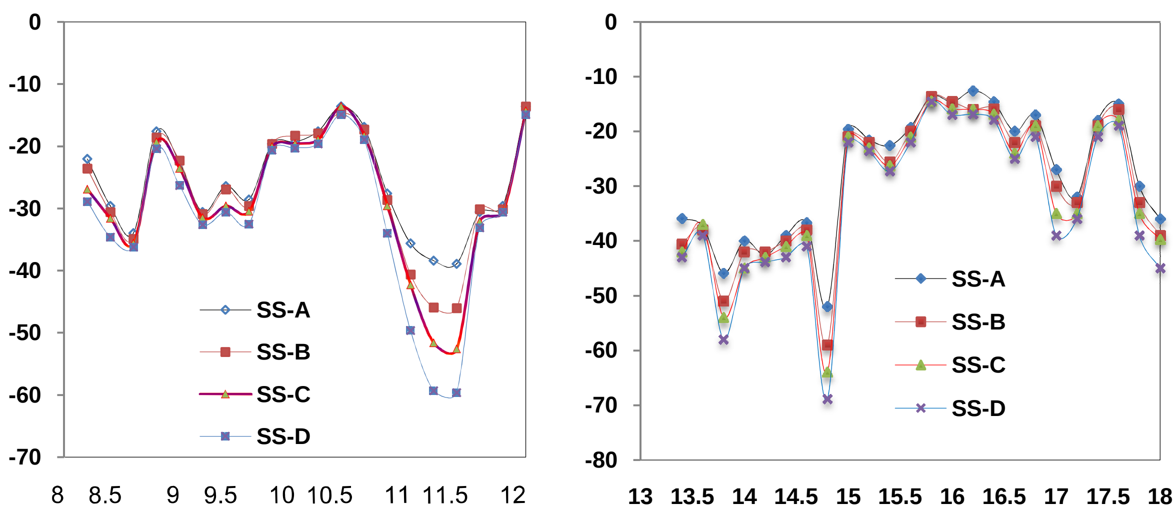



**Fig. 6 Shielding effectiveness of polyaniline thin films in X and Ku-band.**

$$\text{Shielding Effectiveness (S.E.)} = 10 \log \frac{Pt}{Pi}$$

Where, $P_t$ is the transmitted power and $P_i$ is the incident power.

Using this equation the plot of shielding effectiveness in dB as a function of frequency has been plotted in fig. 6. From fig. it is seen that in X-band shielding effectiveness is maximum in the frequency range 11.2–11.6GHz and it is about 40-60db. Below 11GHz the average value of shielding effectiveness is 20-30db. Shielding effectiveness is higher (~70db) at 14.8GHz and at 13.6GHz, it is ~60db in Ku-band. Above 15GHz the shielding effectiveness is less and slightly it is increases with frequency from 16GHz. Thickness dependent effects are observed at 11.5GHz in X-band and at 14.8GHz in Ku-band. In both X and Ku-band, frequency dependent effects are observed. PANI thin films have better shielding effectiveness in Ku-band than X-band.

## CONCLUSION

The PANI thin films change the transmission and reflection properties of SS substrate. The properties are current, thickness and frequency dependent. It is seen that the differences are observed in change in transmittance and change in reflectance between X-Band and Ku-Band. The current during deposition dependent changes are observed. Thickness dependent changes are not very prominent. These types of films can be used as a reflector antenna coating especially Ku-Band than X-Band. The larger dispersion is observed after moisture exposure. PANI thin films have better shielding effectiveness in Ku-band than X-band. Frequency dependent effects are observed. For microwave antenna application, the transmittance, reflectance and conductivity and shielding effectiveness of PANI thin films are important aspects to choose the frequency range for the antenna.

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