



SYNTHESIS, CHARACTERIZATION AND MICROWAVE ABSORPTION STUDIES OF POLYANILINE-MoO₃ COMPOSITES

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Abstract: Increase of crystallinity and conductivity of polymers by inserting metal oxide materials in to polymer matrix integrates the technology of composite materials. Polyaniline (PANI) has received much attention because of its unique reversible proton doping, high electrical conductivity ease of preparation and low cost. The demand of high quality materials for electromagnetic compatibility is alarmingly increasing. insitu polymerization for Polyaniline-MoO₃ (PANI-MoO₃) composite material. PANI with different weight percentage of MoO₃ constitutes different PANI-MoO₃ to know detailed changes. These composites were characterized by using FTIR, SEM and XRD tools. Microwave absorption properties such as Return loss and Shielding Efficiency were evaluated from S parameter measurements. The new material exhibits very good electromagnetic interference shielding efficiency (EMI-SE) compared to previously developed PANI based composites and is a potential candidate for EMI shielding.

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1. INTRODUCTION

Microwaves (30 MHz-30 GHz) have become very important for today's human life and which are extensively used in radar, transmission of television programmes, wire less communication, astronomic research, radio spectroscopy and many other practical fields. Microwave radiations also leaves harmful effects on human body organs if exposed for a Considerable time these effects include increase in heart beats weakening of immune systems, rearrangement of proteins including DNA increasing possibility of leukemia, sterility, cataract cancer etc. therefore stringent environmental stipulations are nowadays being enforced [1]. The electromagnetic compatibility (EMC) is an essential requirement to be fulfilled by the electronic devices/systems. Electromagnetic interference (EMI) is a disturbance on electronically controlled systems for medical & industrial instruments; EMI has become a matter of crucial concern. The rapid growths in cellular phones & wireless devices have further added to problem of EMI. The common problems due to EMI are malfunctioning of devices, formation of false/ghost images, inconsistent radar signals etc. Therefore operation of cellular phones & other wireless devices are prohibited in hospitals, bank, ATM, aero planes etc. Because of these problems microwave absorbers are gaining immerse importance in controlling the wave pollution [2-5] and ensures the undisturbed functioning of the equipment in presence of internal electromagnetic waves. Appropriate microwave absorbing materials in appropriate places in electronic equipment controls the excessive self-emission of electromagnetic waves and ensures the undisturbed functioning of equipment. Achieving the EM wave conditions is referred as Electro-magnetic compatibility (EMC). Radar signature reduction is another area where these microwave absorbers are employed for effective counter measures against radar surveillance [6-7]. Microwave absorbers stick on metallic target, absorb radar microwaves and prevent them from returning back to the transmitting/receiving antenna at the radar unit. Thus defeating the detection by radar.

2. EXPERIMENTAL

2.1 Materials & Methods

All Chemicals used were analytical reagent (AR) grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ((NH₄)₂S₂O₈), Hydrochloric acid (HCl),



Molybdenum trioxide (MoO_3) and were procured from Sigma Aldrich and were used as received.

0.1 mol of aniline was dissolved in 1 M HCl to form aniline hydrochloride. Molybdenum trioxide (MoO_3) is added in the weight percent of 10,30, and 50 to aniline hydrochloride solution with vigorous stirring in order to keep the Molybdenum trioxide suspended in the solution. To this reaction mixture, 0.1 M of ammonium persulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ which acts as the oxidant was added slowly with continuous stirring for 4 – 6 hours at $0 - 5^\circ\text{C}$. The precipitate powder recovered were vacuum filtered and washed with water and acetone. Finally the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In this way 3 different polyaniline MoO_3 composites with different wt% of MoO_3 (10, 30 and 50) in polyaniline have been synthesized.

Preparation of Pellets

Varied concentrations of prepared composites were pressed under pressure for its pellet form. The test samples to be used were prepared in pellet form of diameter 10mm and X-band dimension by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

2.2. Characterization

The structures of as prepared polymer composite were studied by X-ray diffraction using Phillips X-ray diffractometer (PW3710) with $\text{Cu K}\alpha$ as source of radiation. Morphology and bonding of the above polymer composites were studied by Phillips XL 30 ESEM and Perkin-Elmer 1600 spectrophotometer in KBr medium tools respectively. The composite samples were fit in to desired rectangular shape of size of x-band for microwave measurement using the (HPES 6719) vector network analyser (VNA). The scattering parameter is calculated using the Nicholson -Rose method.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Figure 1(a) Shows X-ray diffraction pattern of polyaniline. Careful analysis of X-ray diffraction of polyaniline suggests that it has amorphous nature with a broad peak centered on $2\theta \approx 26.40^\circ$.

Figure 1(b) shows the X-ray diffraction pattern of polyaniline – MoO_3 composite with 50 wt % of MoO_3 in polyaniline. It is seen from the figure that, the peaks of MoO_3 indicates the



crystalline nature of the composite. By comparing the XRD pattern of composite with that of PANI, the prominent peaks corresponding to $2\theta = 33.51^\circ$, 56.04° and 67.05° , are due to (010), (020), (030) planes of MoO_3 [8]. By comparing the XRD patterns of the composite, it is confirmed that MoO_3 has retained its structure even though it is dispersed in PANI during the polymerization reaction.

3.2. Infrared study

Figure 2 (a) shows the IR spectra of polyaniline where the transmittance is plotted as a function of wave number (cm^{-1}). Careful analysis of the spectra reveals the presence of intensity peaks 3417.58cm^{-1} , 2923.26cm^{-1} , 1574.77cm^{-1} , 1489.81cm^{-1} , 1300.17cm^{-1} , 1118.23cm^{-1} , 817.61cm^{-1} and 502.12cm^{-1} . The spectra show the presence four intense bands at 1574.77cm^{-1} , 1489.81cm^{-1} , 1300.17cm^{-1} and 1118.23cm^{-1} . The peak at 3417.58 is due to secondary amine, 2923.26 is CH_2 a symmetric stretching. The intense peaks at 1574.77cm^{-1} and 1489.81cm^{-1} may be attributed due to the presence of quinoid ($\text{N}=\text{Q}=\text{N}$) and benzenoid ($\text{N}=\text{B}=\text{N}$) ring stretching. 1300.17cm^{-1} is due to N-H deformation, 1118.23cm^{-1} is because of silicate Si-O bond stretching and 502.12cm^{-1} is out of plane bending.

Figure 2 (b) shows the IR spectrum of pure MoO_3 . The important peaks observed in MoO_3 are 2345.80cm^{-1} , 991.19cm^{-1} , 863.51cm^{-1} and 563.31cm^{-1} . The presence of MoO_3 is due to the characteristic stretching frequency observed at 563.31 (M- O) cm^{-1} .

Figure 2 (c) shows the IR spectra of polyaniline – MoO_3 composite (50 wt % of MoO_3 in PANI). The prominent peaks that are observed in polyaniline – MoO_3 composite are 3423.07cm^{-1} , 2922.64cm^{-1} , 1578.08cm^{-1} , 1489.99cm^{-1} , 1308.57cm^{-1} , 1150.06cm^{-1} , 824.54cm^{-1} , 705.13cm^{-1} and 510.35cm^{-1} . By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks are observed at 1150.06cm^{-1} , 824.54cm^{-1} , 705.13cm^{-1} and 510.35cm^{-1} . The data suggest that, there is a Vander walls kind of interaction between the polymer chain and MoO_3 [9-11].

3.3. Scanning Electron Microscope

Figure 3 (a) shows the SEM micrograph of conducting polyaniline synthesized by chemical oxidative method. It can be clearly seen that the micrograph of polyaniline is branched and homogeneous. Since Hydrochloric acid is used as protonic acid in the preparation of polyaniline, the presence of microcrystalline structure can be seen. The presence of microcrystalline structures in polyaniline in this particular sample can be confirmed from



XRD studies. Since conducting polymers are very sensitive to the temperature, due to the interaction between electron and the sample, considerable amount of heat is generated which causes the development of small crackening in the sample during SEM recording. A granular morphology of the microcrystalline structures is measured and is found to be about 312 nm in diameter for polyaniline which is consistent with other reports [12-18]. The contrast in the image is a result of differences in scattering from different areas of the surface as a result of geometrical differences.

Figure 3 (b) shows the SEM image of pure MoO_3 and it is observed to have the rectangular like shape. The average length is found to be of 392.1 nm. These structures play an important role in enhancing the electrical property of the composites

Figure 3(c) shows the SEM micrograph of polyaniline- MoO_3 composite with 50 wt% of MoO_3 in polyaniline, the SEM image reveals the presence of MoO_3 particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of MoO_3 so dispersed in polyaniline has been observed. Also fibrillar morphology is observed in the composite. The size of this crystallite is around 356.5 nm. The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and MoO_3 .

3.4. Microwave study

3.4.1 Return loss

Figure (4) shows the variation of return loss spectra at X-band frequency for the composites samples 10 wt% to 50 wt% of MoO_3 in polyaniline. These composite shows increase in return loss value as frequency increases and also observed that the 50wt% of MoO_3 in PANI shows maximum return loss this may be due to resonance. In case PANI- MoO_3 the return loss varies from 1dB to 18dB. The return loss spectra also show multi band spectra this is due to the resonance between the material and the applied frequency.

3.4.2. Electromagnetic Interfacing-shielding effectiveness

Figure (5) shows the variation of EMI-SE at X-band frequency for the composites samples 10 wt% to 50 wt% of MoO_3 in polyaniline in the frequency range 8.2 to 12.4 GHz. The EMI-SE spectra of all the sample shows multiple bands with significant variation in the whole frequency range used in the present work. However the EMI-SE values is decreased with the increase of wt% MoO_3 in PANI and maximum value observed at higher frequency side, and



also observed that different compositions shows different EMI-SE values but varies from 80 to 95. This may be due to the orientation of domains remained perpendicular to the direction of wave propagation. The obtained data reveals that the relative SE is higher at particular frequency range.

CONCLUSION

The PANI-MoO₃ composites with different weight percent ratios have been successfully synthesized. Microwave absorption properties are investigated. It is found that the absorption properties in the composites are greatly improved with increasing MoO₃ in PANI. The composite with wt % of MoO₃ in PANI shown multi band maximum absorption in X-band frequency

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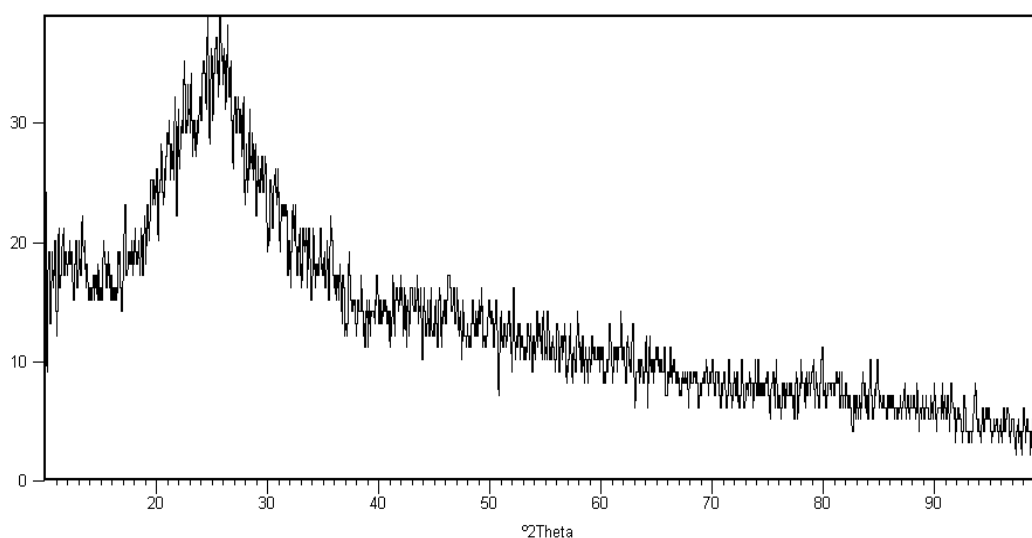


Figure 1(a) X-ray diffraction pattern of Polyaniline

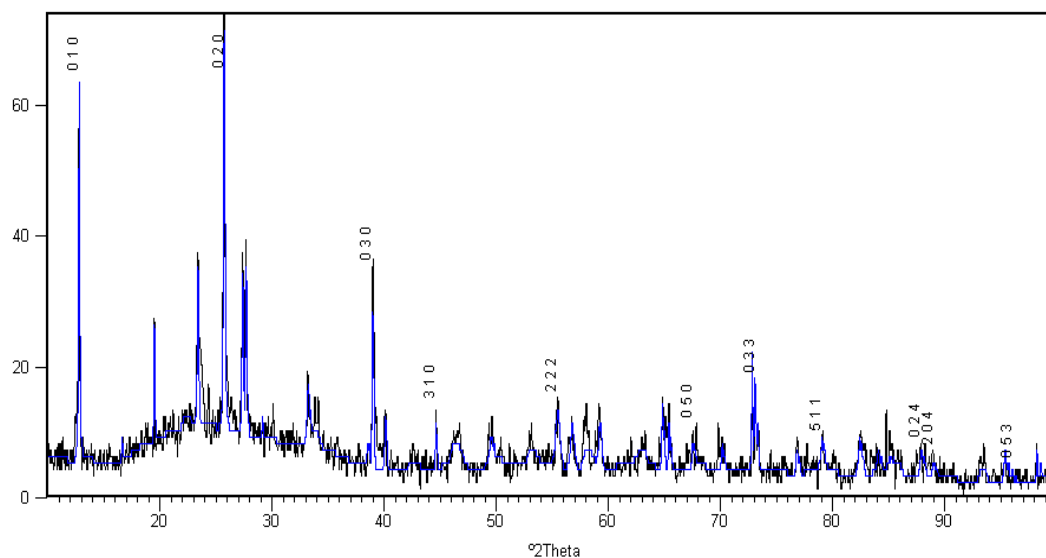


Figure 1(b) X-ray diffraction pattern of Polyaniline – MoO₃ composite

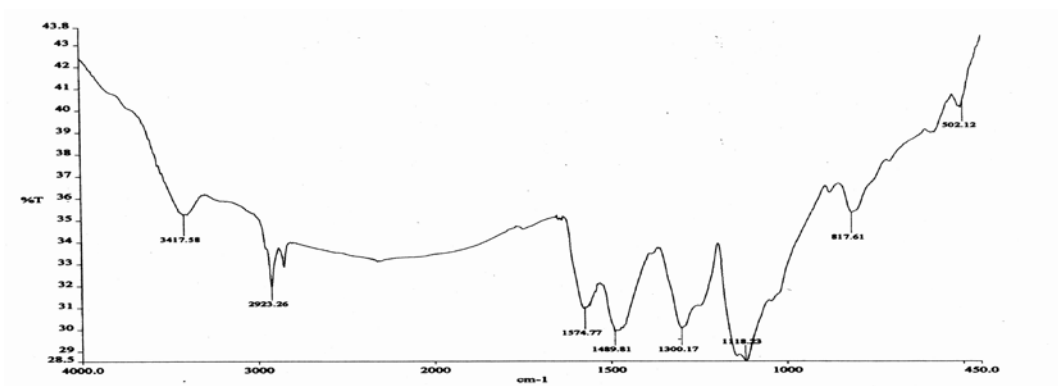


Figure 2(a) FTIR spectra of pure Polyaniline

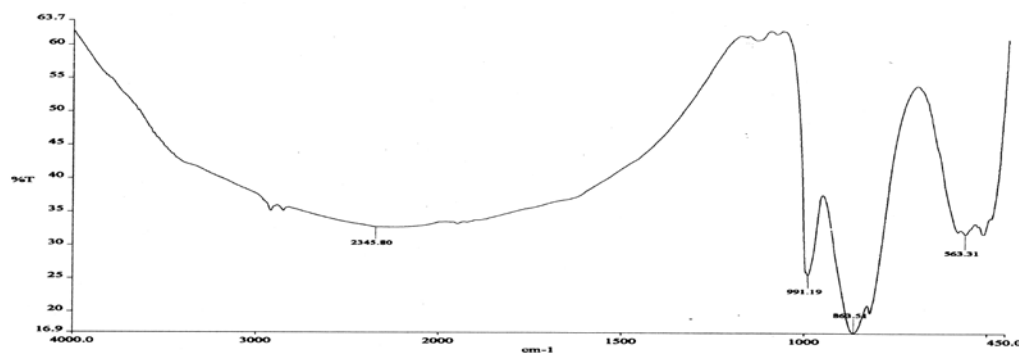


Figure 2(b) FTIR spectra of pure MoO₃

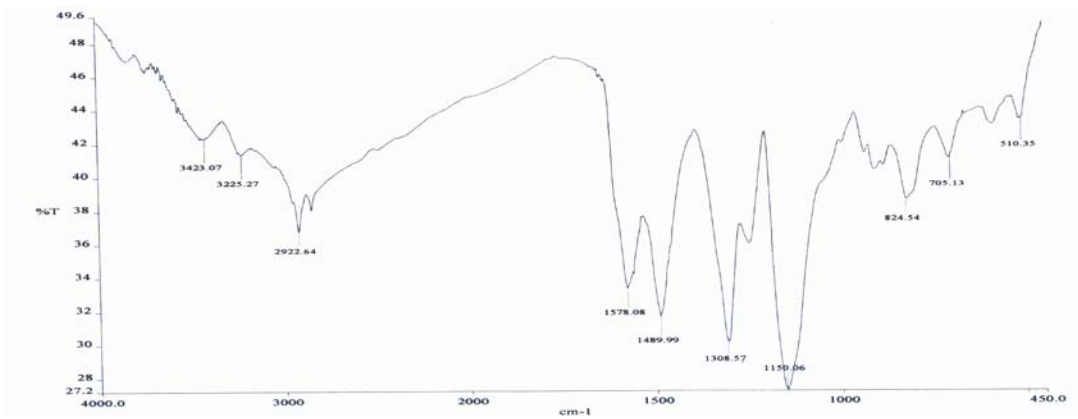


Figure 2(c) FTIR spectra of Polyaniline – MoO₃ composite (50 wt %)

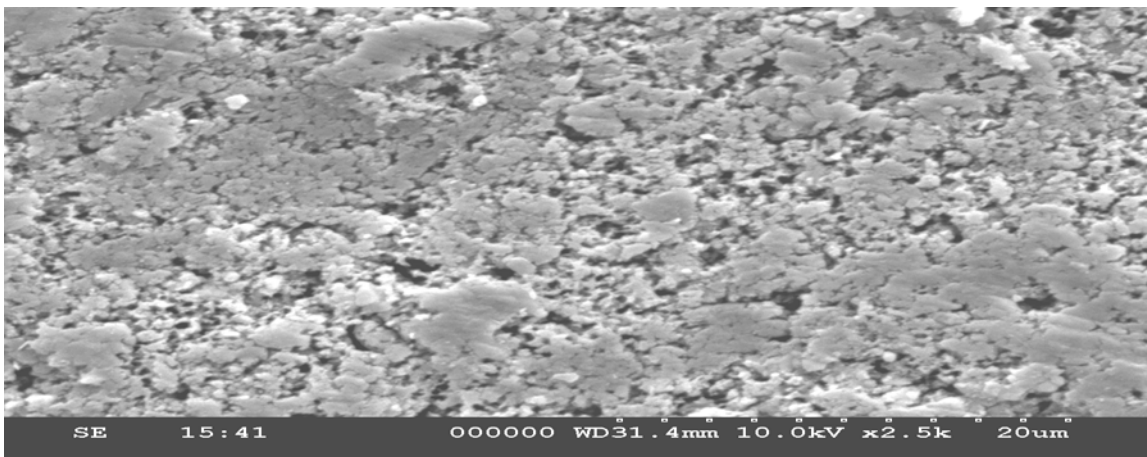


Figure 3 (a) SEM Micrograph of Polyaniline

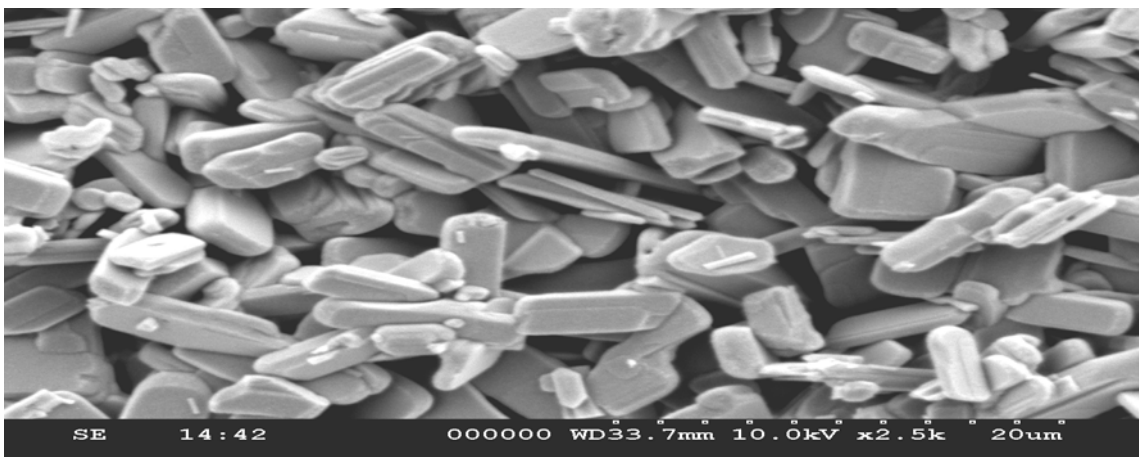


Figure 3(b) SEM Micrograph of MoO₃

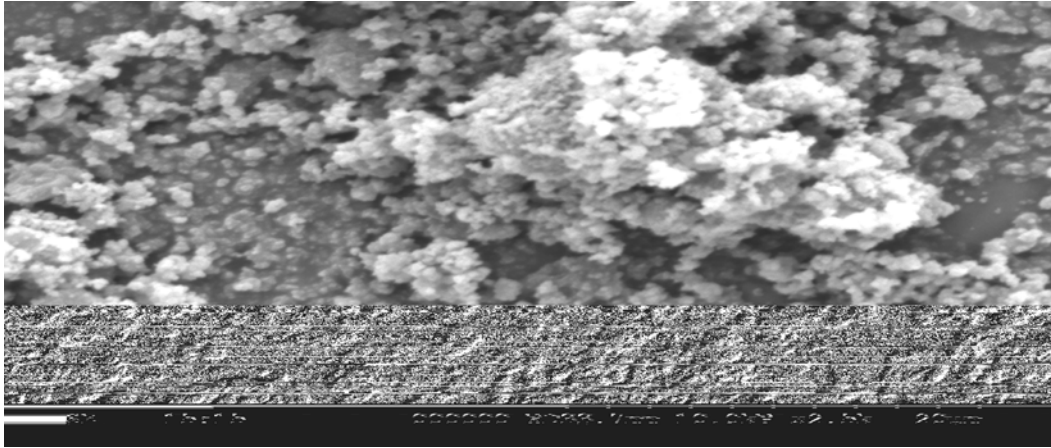


Figure 3(c) SEM Micrograph of Polyaniline - MoO_3

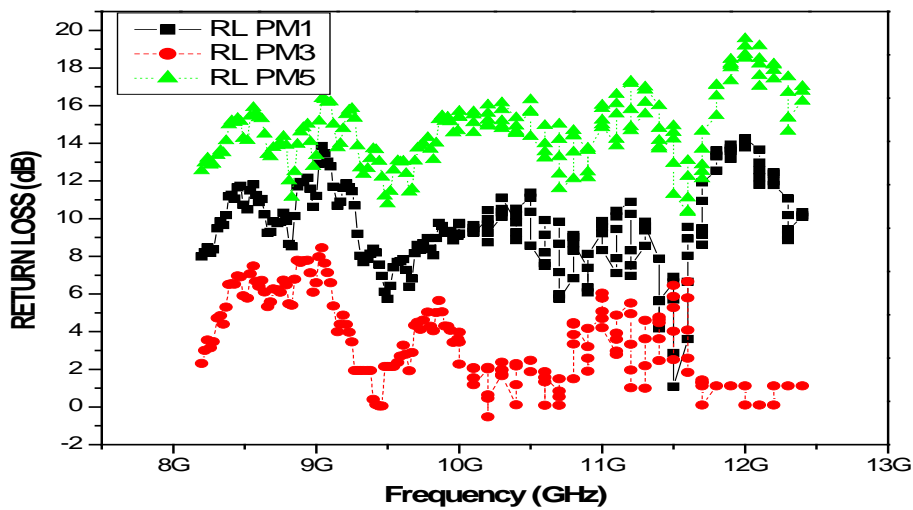


Figure (4) Variation of return loss Vs frequency (PANI- MoO_3)

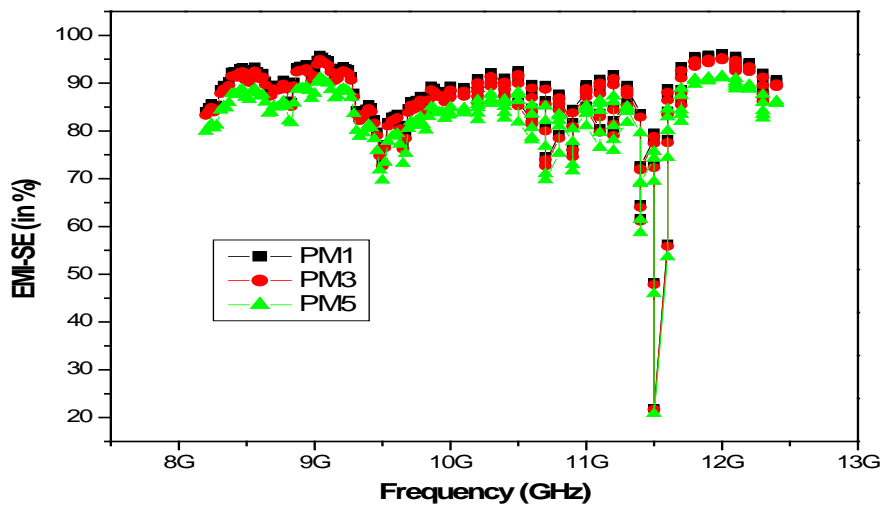


Figure (5) Variation of EMI-SE Vs frequencies (PANI- MoO_3)