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# Microwave characterization of polyaniline prepared via agitation-free self-stabilized dispersion polymerization

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## Abstract

Processible forms of Polyaniline require special attention because of its inherent nature of forming poor dispersions in organic and aqueous solutions due to morphological distortions caused by conventional means of mechanical agitation of reaction mixture. In this work the authors have prepared Polyaniline samples by self-stabilized dispersion polymerization in the absence of mechanical agitation. The authors have also prepared Polyaniline samples via other chemical routines as reference samples. The dielectric properties of the products were analyzed in low frequency (20Hz-2MHz) and in C-band (4GHz-8GHz) of microwave frequency. The C band complex permittivity measured using cavity perturbation method is in good agreement with simulation results obtained from CST Microwave Studio, hence substantiating the material properties. The skin depth and conductivity of the material is measured. The material exhibits better conductivity when prepared under agitation free environment. Such made material is investigated for its potential use as a microwave absorber. The return loss and gain of the polymer pellet made using the proposed synthesis is investigated. The return loss seems to have good impedance matching. The radiative gain of the polymer pellet is exhibiting loss due to the high loss tangent associated with the material at the resonance frequency. Morphological analysis was done by taking SEM images of the samples to confirm the relationship between material quality and the properties obtained. The material can be used to fabricate microwave absorbers.

## 1 Introduction

usage of metal alternatives for electronics applications have become promising since the discovery of conducting polymers[1]. Conducting polymers are special synthetic materials with properties like good electrical conductivity, thermal stability, flexibility, mechanical strength, environmental stability etc. These properties make them suitable in arenas like electrical conduits in corrosive environments, flexible transparent conductors, charge

dissipater for anti-static coatings, sensors etc[2-5]. Applications of conducting polymers can be extended to microwave electronics with typical usage as EMI shielding materials, radar absorbing materials, frequency selective surfaces, flexible antennas for body area networks etc[6-9]. Among many Intrinsically Conducting Polymers (ICP), Polyaniline (PANI) became very popular owing to its ease of preparation, reversible electronic characteristics with simple acid/base chemistry and better environmental stability. Since the discovery of PANI, variants of PANI with better properties are being developed[10-11]. The challenge inherent with PANI is in its conductivity and processability enhancement. The poor processability arises from the reduced degree of freedom resulting from the pi-conjugated polymer backbone of conducting polymers in general. But the pi-conjugation wherein electron probability gets distributed along the polymer backbone is the core of electrical conductivity in these synthetic metals. This delineates a trade-off between conductivity and processability of these materials. There has been a trend in recent years towards the preparation of PANI in nanoscale form[12-15].

When compared with bulk conducting polymers, nanoscale conducting polymers display better performance in applications by virtue of the unique properties arising from their size such as high conductivity, large surface area, and light weight[16-17]. These nanostructures can be synthesized by many methods such as soft-template methods, hard template methods, controlled solution synthesis, electro-spinning technique, self-assembly etc[11]. This work is an attempt to quantify and compare the microwave property variation for PANI samples prepared by self stabilized dispersion polymerization in agitation free environment with respect to other synthesis routes.

It has been reported earlier that stable PANI dispersions in aqueous medium can be made with PANI nanofibres prepared from polymerization of aniline monomer without mechanical agitation[18-19]. PANI preferentially looks for nanofibre configuration in undisturbed reaction mixtures. In the presence of stirring, the initial nanofibres get agglomerated as stirring induces collision of initial nucleates which act as the reaction

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centres. This causes heterogeneous nucleation and makes agglomerated particulates of initial nanofibres as the final product. These particulates settle down after reaction and pose difficulty in the solution processing of PANI. When the reaction is not stirred, the PANI nucleates grow radially outwards as nanofibres due to homogeneous nucleation. Such made PANI are easily dispersible into stable suspensions at high concentrations in aqueous media after purification indicating the absence of stirring induced agglomeration. In the standard polymerization reaction it is found that during PANI formation, undesired branching and premature termination can cause poor quality samples containing PANI in composite morphologies. In such cases, ortho-coupling of aniline rings instead of para-coupling cause problems and give way to many low molecular weight oligomers and unwanted crosslinking. S. H. Lee et al has shown that PANI nanofibres can be easily prepared by self-stabilized dispersion polymerization (SSDP) in aqueous-organic heterogeneous mixtures[20-21]. In such a heterogeneous mixture, anilinium hydrochloride acts as an interfacial stabilizer between the two media. When the reaction proceeds, the organic media isolates the oligomers from the reaction sites in aqueous media, making PANI less vulnerable to side linkages. This in turn helps to reduce agglomeration and improves the quality of samples.

In this paper, a comparative study of Polyaniline samples synthesized via different routines is done with an attempt to combine self-stabilized dispersion polymerization and eliminating mechanical agitation of the reaction mixture thereby inhibiting the heterogeneous nucleation of PANI nucleates. The developed material is investigated for its low frequency and microwave properties and its property dependency on synthesis routine, which is the aim of this study. An attempt to study the radiative properties of such made material for use as polymer antennas is also investigated. The antenna shows good impedance matching at the design frequency in C band.

## 2 Experimental

### Sample Preparation

All chemicals used were of analytical grade from Merck Chemicals. Four samples namely PANI-1 (conventional routine), PANI-2 (without mechanical agitation), PANI-3 (using SSDP), PANI-4 (proposed) were prepared. It has been previously demonstrated that the conductivity of polyaniline with organic acids like Camphor sulphonic acid (CSA) or Naphthalene sulphonic acid (NSA) is many orders higher than that obtained with inorganic acids[22]. For a comparative study between synthesis methods, doping with any inorganic acid would suffice. Hence hydrochloric acid was chosen as the dopant.

The reactants were pre-cooled to 0°C. Aniline monomer (5ml) was dissolved in 1 Molar aqueous acid (HCl) and mixed with chloroform (aqueous acidic aniline solution: chloroform=2:1). The mixture was kept under constant stirring at 300 RPM in a mechanical stirrer until the mixture became a turbid colloid. The temperature was kept constant at 4°C. Ammonium Persulphate taken in aqueous acidic solution was then added rapidly to the above colloid and stirred for 2 minutes. The mechanical stirring was then stopped and the reaction mixture was allowed to stand for 12 hours. The PANI obtained was filtered, washed with water, dopant acid and acetone. The sample was dried at 50°C in oven for 4 hours, grounded to fine particulates and stored in polyethylene covers.

The powdered samples were pelletized into standard 13mm diameter cylindrical pellets of height 1.25mm for low frequency dielectric characterization. Cylindrical samples of average volume= 3.8443mm³ were prepared from the same 13mm pellet samples for maintaining constancy in packing fraction for microwave dielectric parameter extraction.

### Dielectric Properties

The dielectric property measurement was performed at two different frequency ranges for better understanding of the underlying phenomena in the different methods of preparation. In both cases either the complex impedance or the complex permittivity is estimated from which conductivity, skin depth, loss tangent, absorption coefficient etc. can be determined.

### Low Frequency Characterization

The low frequency dielectric properties in the range 20Hz to 2MHz was measured by the method proposed by A Fattoum et al.[23], using Agilent E4980A Precision LCR Meter. The pellet samples were inserted into the dielectric test fixture and the measurement was carried out to obtain the complex impedance of the material in the frequency range. The dielectric constant and conductivity of the samples were computed as,

$$\epsilon_r = \frac{X d}{2\pi\epsilon_0 A (R^2 + X^2)}$$

$$\sigma = \frac{R d}{A (R^2 + X^2)}$$

Where f= frequency of measurement, A= cross-sectional area of pellet, d= thickness of pellet, $\epsilon_0$ = free-space permittivity, R= resistance of pellet and X= reactance of pellet.

### Microwave Characterization

The microwave dielectric characterization was done in the C band (4GHz-8GHz) frequency range using R&S ZVB20 vector network analyzer (VNA). It has been previously demonstrated that polyaniline doped with lower order inorganic acids will exhibit lesser dielectric loss compared to higher order organic acids due to lesser electron delocalization. Hence the resonant cavity perturbation method was used to estimate thematerial properties[24]. As the sample was expected to be dissipative, the sample height taken was lesser than the height of the cavity. This induces depolarization fields inside the sample whose effects are compensated in the measurement by using depolarization correction factor for

cylindrical samples[25]. The sample was inserted into C-band rectangular cavity operating in $TE_{10p}$ mode through a non-radiating slot in the cavity wall. The frequency and Q-factor shifts for each resonant frequency were measured by automated measurement setup. The complex permittivity was calculated by solving the following equations.

$$\frac{f_s - f_0}{f_s} = \left\{ N_e \left( \epsilon_r^2 - 2\epsilon_r - \epsilon_i + 1 \right) + 1 - \epsilon_r \right\} \left\{ \frac{2V_c}{V_s} \right\}$$

$$\frac{1}{Q_s} - \frac{1}{Q_0} = \left\{ \epsilon_i - 2N_e \epsilon_i (\epsilon_r - 1) \right\} \left\{ 4\frac{V_s}{V_c} \right\}$$

Where $N_e$ =effective depolarization factor, $f_s$ =resonant frequency of cavity with sample, $f_0$ = resonant frequency of cavity without, $Q_s$ =Q-factor of cavity with sample, $Q_0$ = Q-factor of unloaded cavity, $\epsilon_r$ =real part of permittivity, $\epsilon_i$ =imaginary part of permittivity, $V_s$ =sample volume, $V_c$ =cavity volume.

The measured microwave properties of the PANI samples were confirmed by the following procedure. As shown in Fig. 1, a 13mm diameter cylindrical pellet of height 1.25mm was fed through a microstrip proximity coupling line of 50Ω impedance. The return loss of the setup was measured using R&S ZVB20 VNA. The same setup was simulated in CST Microwave Studio with the material properties of the pellet set to that measured using cavity perturbation analysis.
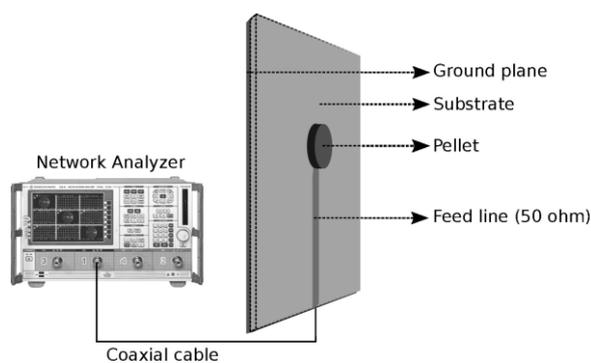


*Polymer Pellet Characterization*

The polymer pellet was tested for its radiational capabilities. When the material is investigated for absorptive applications, the mechanism of wave propagation through the material should be understood. The return loss of the proximally fed polymer pellet is estimated using R&S ZVB20 VNA.

*Morphological Characterization*

The morphology of the prepared samples were analyzed with the help of Scanning Electron Microscope (SEM) images. The morphology determines the electrical and mechanical properties of the material. It gives a qualitative assessment of the effects of different methods of preparation on the material properties.

## 3 Results and Discussion

The behaviour of materials towards electromagnetic fields can be entirely attributed to the dependency of dielectric properties over the frequency of incident radiation. A time varying electromagnetic field induces oscillating dipoles in a material composed of permanent dipole moment, upon incidence. Thus the power in the incident radiation propagates through the medium by polarizing the material. Hence the extent to which the medium can be polarized determines the energy storage capacity of the material. Apart from this, a portion of power used to oscillate the dipoles is lost as heat. Radar absorbing materials utilize this property to avoid unnecessary reflections of incident electromagnetic pulse. In the case of conducting polymers, the charge delocalization effect creates free charges. This accumulation of surface charges brings discontinuity in the field induced inside the material. The reduced field strength in the material is accompanied by reflection of a part of incident field from the surface charge sheet present at the conducting polymer boundary. As stated earlier, Polyaniline with HCl dopant contain charges with lesser mobility. Due to this less conductivity of HCl doped PANI samples; they act as lossy material instead of a good electrical conductor, albeit electrical conductivity can be enhanced manifold by dedoping Polyaniline and reprotonating it with CSA or NSA. Thus field do propagate through PANI giving rise to the real part of permittivity in contrast to highly conducting reprotonated PANI samples in which case the constitutive parameters become frequency independent from dc to microwave.
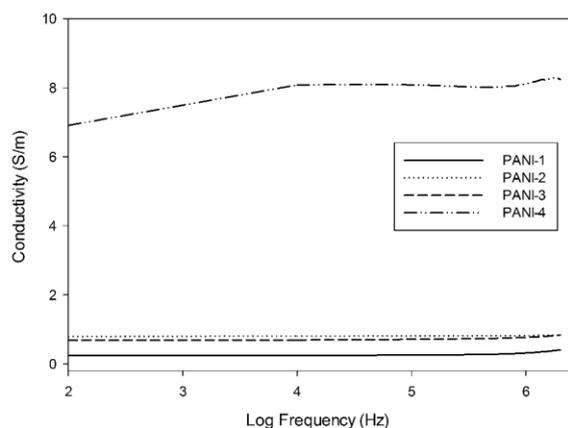
*Dielectric Characteristics*
    a)   Low Frequency

Electronic interactions present in conducting polymers arise out of three processes: intra-chain, inter-chain and inter-domain. A material which is below the percolation threshold contains conductive chains and domains separated by potential barriers. This situation is accompanied by reduced electron hopping probability for chain to chain or for domain to domain transport.
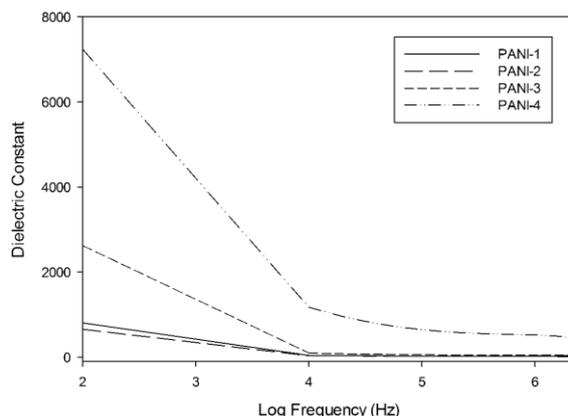


In such cases the material under test (MUT) contains a capacitive component and the complex impedance will have a negative imaginary part at the measured frequency.

For better conductivity, the material needs to be percolated above the threshold and then the samples will behave inductively. Hence at very low frequencies, it is convenient to measure complex impedance offered by the MUT and then extract the dielectric parameters such as conductivity, dielectric constant, skin depth, loss tangent etc. which are manifestations of the complex permittivity.



In short, low frequency dielectric characterization can be expressed in two parameters: conductivity and dielectric constant from the real and imaginary parts of complex impedance respectively. The dielectric constant and conductivity variations against log frequency in the range 20Hz-2MHz are plotted in Fig.2 and Fig.3 respectively. From Fig.3 it is evident that the new method gives very good conductivity at these low frequencies and the material can be considered inductive load which is an indication of better percolation. Also the dielectric constant is greater than that for the other samples. Better dielectric constant indicates better energy storage capacity of the material at these frequencies. It can be seen that the dielectric constant is very high at low frequency. This is due to relaxation process and electrode effects due to polarization between surfaces [26, 27].
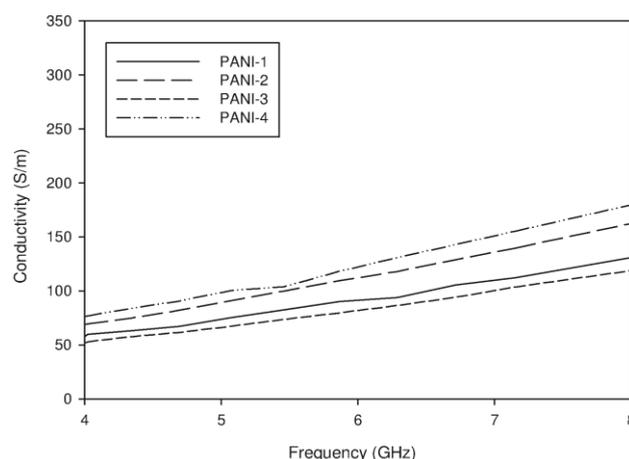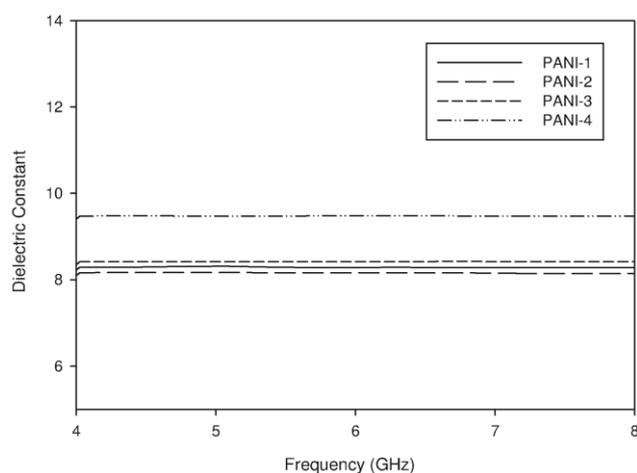




a) Microwave Frequency

The microwave material properties evaluated in the C-band indicates that the dielectric constant maintains less variation while the conductivity increases with frequency in the C band as seen from Fig.4 and Fig.5. This increase can be attributed to the fact that the dipolar oscillations may slip out of phase when the incident field is fast varying. Hence as the frequency increases, the polarization can be resolved into an in-phase component and an out-of-phase component with respect to the incident field, causing thermal dissipation of microwave energy. The tangent of the angle between these two fields give the loss tangent which is a direct measure of the losses inherent in these materials. In Fig.6 the skin depths at C-band for the four samples are compared. It can be seen that it is the lowest for PANI-4. The skin depth decreases with frequency due to the increase in conductive losses alongside dielectric losses. These behaviour are comparable to that seen from previous work in microwave characterization of PANI[28].
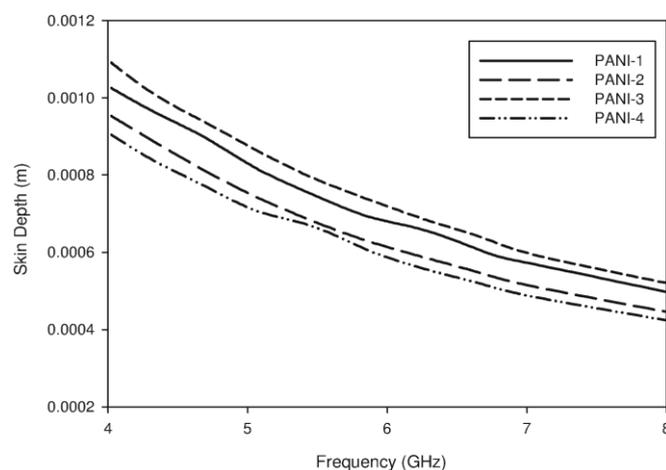


*Absorption Characteristics*

The evaluation of material properties thus obtained was done using circuit simulation in CST Microwave Studio. It can be seen from Fig.7 that the simulation results are in good congruency with the measurement. For comparison, the return losses of each of the four samples

kept on the microstrip feedline are also projected onto Fig.8. Apart from the differences in conductivity, the only notable change among these samples is in the dielectric constant. The pellet on the feedline has a resonance at 5.5GHz. This resonance is at a lower frequency for the sample prepared by new method, when compared with the other three samples. This happens due to an increase in the effective electrical dimensions of the pellet with the increase in the dielectric constant and thus lowering the resonant frequency. From material properties, it has to be noted that the material is not strictly dielectric and that it has some losses. Results indicate that the radiative gain of the polymer pellet on microstrip feed setup is very small (-3.5dB) and that the sharp dip in return loss at 5.5GHz is due to high absorption faced by the coupled field in the lossy dielectric. Thus the power at that particular frequency from the feedline is not radiated to freespace but dissipated in the pellet itself. This proposes applications in the field of radar absorbing materials which selectively absorb power in a desired frequency band.
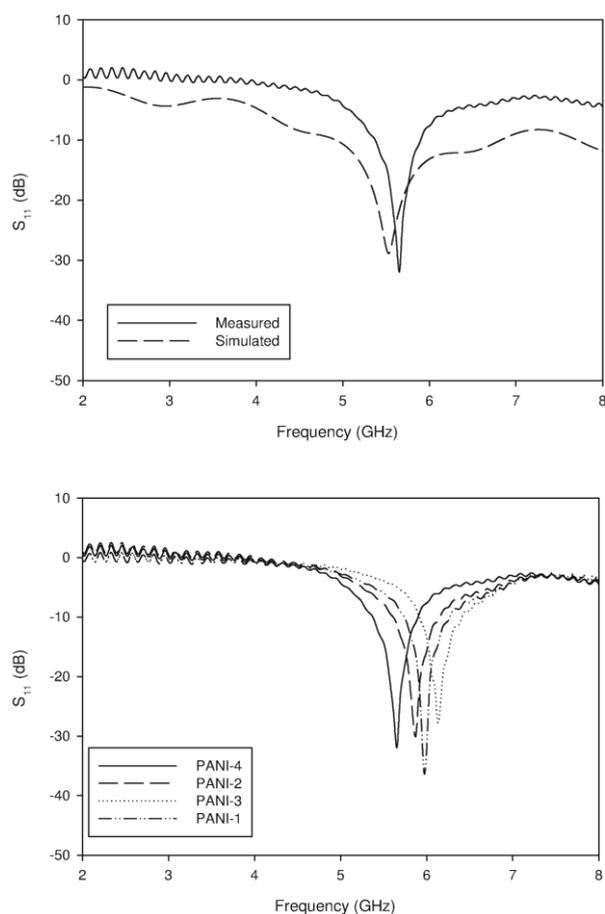




*Morphological Characteristics*

The morphological properties of a material has significant role in determining its macroscopic properties. In case of conducting polymers, the bulk conductivity is related to the morphology of the material. This determines the quality of the material. When the particle size decreases, the surface area increases which will significantly improve the inter-chain and inter-domain

charge transport. Thus it is required that the particle size be reduced. From Fig.9, it can be seen that the size reduction achieved in PANI-4 is better compared to the samples prepared via other methods. This difference will be more prominent in the case of low frequency conductivity.



(a)       (b)

(c)       (d)
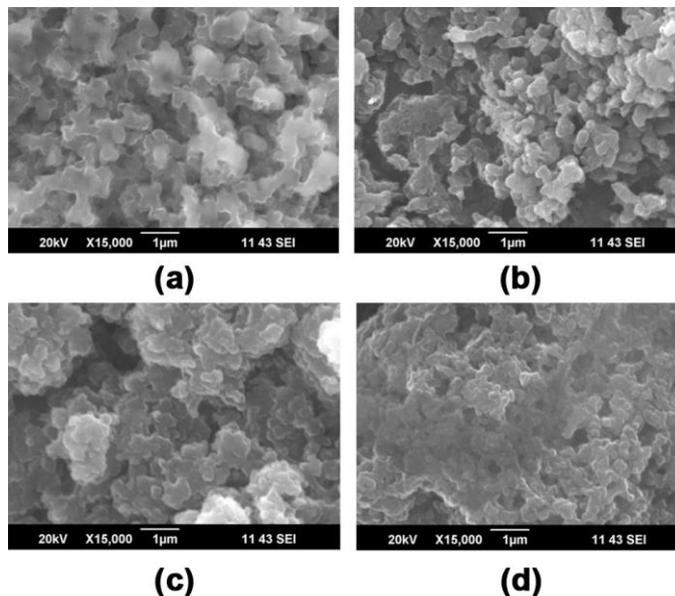
This is because of the fact that the increased surface area aids better conductivity and can be seen in Fig.3 which places the new sample well above the others in the conductivity ladder. Also it has to noted that for the other samples the particle size is large resulting in lesser contact area and increased inter-chain and inter- domain capacitance. Due to high contact area, PANI-4 will exhibit least inter-chain and inter-domain capacitance and was found to exhibit highest inductive reactance. A high inductive reactance is the indication of coiled structure in the particles. But at microwave frequencies, the capacitive impedance of the other samples are reduced and this makes their conductivity appear higher at these frequencies Conductivity of PANI-4 although ranked highest at these frequencies is slightly reduced which is due to higher inductive impedance offered by the coiled structure. This is not a disadvantage as for use as thin films of polyaniline, a treatment with m-cresol will uncoil the structure and straighten it out, resulting in reduced inductance and higher conductivity.

## 4 Conclusions

The study compares the electromagnetic behaviour of polyaniline samples developed through SSDP in an agitation-free environment and by other methods. The samples give remarkable property enhancement over the samples prepared via conventional procedures for polymerizing aniline. The C-band material properties such as dielectric constant, conductivity, skin depth etc. are compared with the low frequency spectral characteristics of the samples. The microwave properties are confirmed by simulation studies using microstrip feedline. The material is a lossy dielectric. The morphological studies

reveal the cause of better electrical properties obtained in the new method. The PANI samples prepared via this method can be used to develop better processable PANI nanocomposites for various microwave applications like FSS, RAM, wave attenuators etc.

## Acknowledgements

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