# MICROWAVE DIELECTRIC CHARACTERIZATION OF POLYANILINE COMPOSITES

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## ABSTRACT

Dielectric permittivity of polyaniline (emeraldine salt) and its dispersions in epoxy glasses have been investigated in the frequency range between 1 GHz to 18 GHz by using the reflection – transmission method. The observed high value of the dielectric constant is attributed to polarizability originating from a delayed charge transfer between conducting domains with an apparent relaxation at about 6.8 GHz. In composites in which this interaction is interrupted by a non-conducting phase boundary the microwave dielectric polarizability becomes reminiscent of localized states in organic solids.

(Keywords: Microwave dielectric permittivity, Polymer composites, Polyaniline)

## INTRODUCTION

Intrinsically conducting polymers such as polyaniline exhibit unusually high polarizability and high dielectric constant, which extends into microwave range. Typically, the frequency dependent dielectric permittivity in organic polymers is dominated by reorientation of molecular dipoles [1]. Since at higher frequencies the orientational polarization vanishes and the polarizability is determined by the localized electronic states, the relative dielectric permittivity of most organic polymers drops to a low value of about 2-3 approaching a square of the refractive index at optical frequencies. Several investigations of polyaniline salts indicate that its microwave dielectric constant is considerably higher than that of organic solids. It has been reported that the dielectric constant of crosslinked emeraldine salts is proportional to the square of the crystalline domain coherence length and increases from about 800 to about $3.3 \cdot 10^4$ with increasing crystallinity of the macroscopic metallic domains [2]. Investigations by Youngs [3], indicated that the dielectric constant of polyaniline protonated with HCl decreases from about $1 \cdot 10^7$ at 100 Hz to about $1 \cdot 10^2$ at 1 GHz. Naishadham and coworkers measured the permittivity of protonated polyaniline between 2 GHz and 18 GHz in a coaxial line. Their results indicated real permittivity of about 100 at 2 GHz, which decreased to below 2 at 12 GHz [4]. Many of the discrepancies in reported permittivity of conducting polyaniline, especially at microwave frequencies, seem to be a result of variation in composition and application of non-standard measurement protocol. This paper presents the results of microwave permittivity measurements on conducting polyaniline and its dispersions in epoxy glasses by the reflection - transmission method. The transmission – reflection method offers considerable accuracy and can be used in a broad frequency range extending to 20 GHz. The determination of AC conductivity and dielectric constant by this technique can provide valuable insight into electronic structure and electromagnetic properties of polymer composites. The observed dielectric behavior is discussed in

conjunction with the DC conductivity and relaxation originating from the hopping charge transport.

## EXPERIMENT

### Materials

Conducting polyaniline (emeraldine salt, ES) protonated with an organic sulphonic acid was obtained from Aldrich[1]. Die-pressed samples were made from the ES powder, having particle size distributed between 1 μm and 100 μm. The polyaniline material was hot-pressed at 110 °C under pressure of 38 MPa to obtain the final density of 1.32 g/cm$^3$ and DC conductivity $\sigma_{DC}$ of $(3.2 \pm 0.1)$ S/cm. Composites were made by mixing the ES powder with an epoxy resin as the non-conducting phase. The epoxy resin, E−862™ was obtained from Shell. Thermal cross-linking was activated by using a boron trifluoride curing complex, B550™, obtained from Leepoxy Plastics. The curing schedule for composites was 135 °C for 4 h, determined by DSC, followed by a thermo-mechanical analysis and electrical impedance characterization. Samples for the microwave measurements were milled to a cylindrical shape and fitted precisely into a 7−mm beadless coaxial airline.

### Measurements.

A Keithley K2400 current/voltage source was used to measure the DC 4-probe conductivity. The 4-terminal AC low frequency impedance was measured using a HP4194A network analyzer. A 7 mm, beadless coaxial airline having electrical length of 99.95 mm was purchased from Maury Microwave. The airline was connected to a HP8720D network analyzer using an HP85132-60003, 7 mm to 3.5 mm semi-rigid cable kit from Hewlett Packard.
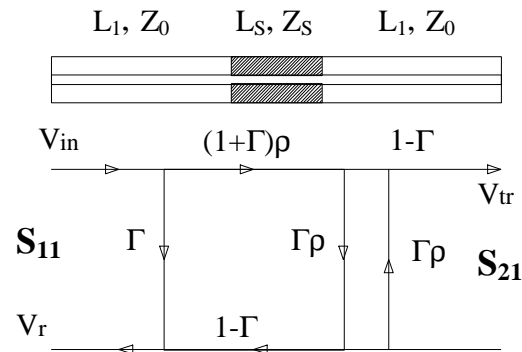


Fig. 1 Two port network flow chart for
     coaxial line filled with dielectric

A signal flow diagram of a two port network for the coaxial line with the dielectric sample of length $L_s$ inserted is shown in Fig. 1 [5]. Since within the dielectric the line impedance changes from $Z_o$ to $Z_s$, incident wave $V_{in}$ will split at each interface into reflected wave $V_r$ and transmitted wave $V_{tr}$. The relationship between the measured complex scattering coefficients $S_{21} = V_{tr} / V_{in}$ and $S_{11} = V_r / V_{in}$, the reflection coefficient $\Gamma$ and the transmission coefficient $\rho$ can be obtained by solving the flow graph of the network using the non-touch loop rule [6]. In Fig.1 there is one path from $V_{in}$ to $V_{tr}$: $(1+\Gamma)\rho(1-\Gamma)$, and two paths from $V_{in}$ to $V_r$ ; one equal to $\Gamma$ and the other equal to $(1+\Gamma)\rho(-\Gamma\rho)(1-\Gamma)$. Then, the solution of the network for the scattered parameters at the sample interface can be expressed as follows:

$$S_{21} = \frac{(1-\Gamma)\,r\,(1+\Gamma)}{1-\Gamma^2 r^2} \quad (1)$$

$$S_{11} = \frac{\Gamma(1-\Gamma^2 r^2) + r(1-\Gamma^2)(-\Gamma r)}{1-\Gamma^2 r^2} = \frac{\Gamma(1-r^2)}{1-\Gamma^2 r^2} \quad (2)$$

wo
$1 - S_{11} 1$

expressions for the reflection coefficient $\Gamma$ and the transmission coefficient $\rho$:

$$\Gamma = K \pm \sqrt{(K^2-1)}, \quad K = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \quad (3)$$

$$r = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} + S_{21})\Gamma} \quad (4)$$

where $r = \exp(-jw\sqrt{m_r^* e_r^*}\, L_s)$, $\Gamma = \dfrac{1-(e_r^*/m_r^*)^{1/2}}{1+(e_r^*/m_r^*)^{1/2}}$ and $e_r^*$, $m_r^*$ are complex permittivity

and permeability relative to a vacuum. Consequently, the materials complex dielectric permittivity can be determined from equations (3) and (4). The phase ambiguity in equation (4) can be resolved by measuring the group delay through the material at each frequency [7]. The magnitude and phase errors of $S_{11}$ increase when $|S_{11}|$ approaches 0 and decrease when approaching 1. The standard uncertainty in $|S_{21}|$ is about $\pm$ 0.05 dB and $\pm$ 0.25° when $|S_{21}| > $ -40 dB, independent of frequency. Thus, the uncertainty is maximum when $|S_{11}|$ is minimum, which occurs when the length of the sample equals $(2n+1)\,\lambda g\,/2$, where $\lambda g$ is a guided wavelength, $\lambda g = $Re $(\lambda o/(\varepsilon_r\mu_r)^{0.5}$. Baker and co-workers developed a convenient procedure that eliminates most of the difficulties associated with phase ambiguity and errors in $L_1$ and $L_2$ that affect the reference planes rotations [8]. Since the procedure works best for low loss dielectrics for which the mechanism of polarization is known, we calculated permittivity from equations (3) and (4). The uncertainties were estimated based on the instrumental error and repeated data from several samples.

## RESULTS

The real and imaginary permittivity of ES is shown in Fig 2 a and b respectively. The dispersion is relatively high. The value of the dielectric constant in Fig. 2a decreases
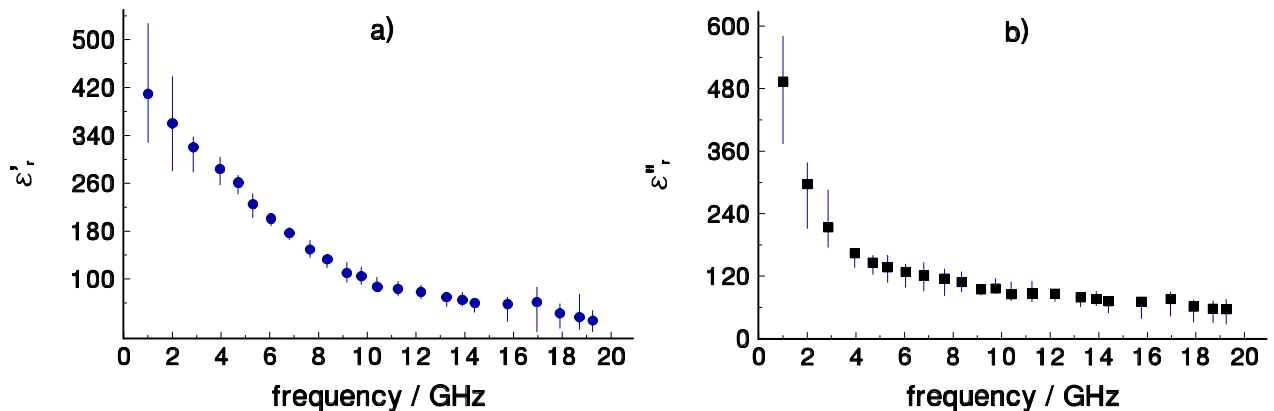


Fig. 2. Dielectric permittivity of emeraldine salt at 22 °C; a) real part, b) imaginary part.

from about 350 at 2 GHz to approximately 35 at 18 GHz. The dielectric loss tangent $e_r^{''}/e_r^{'}$ increases from 0.5 to about 1.3 in the same frequency range. At 6 GHz the complex relative permittivity is $e_r^* = e_r^{'} - ie_r^{''} = 200 - i125$. We note that the corresponding AC conductivity $s_{AC}^{'} = we_r^{''}e_o$ is equal to (0.43 ± 0.08) S/cm, which is smaller than the $(3.2 \pm 0.1)$ S/cm determined at the DC conditions.

Usually, the $s_{AC}^{'}$ increases with frequency and exceeds the $\sigma_{DC}$ due to contributions from dissipative processes associated with the dielectric displacement. If polarization is negligible, $\sigma_{DC}$ may approach $s_{AC}^{'}$. This situation was reported previously for a metallic, 50 % protonated emeraldine salt for which $\sigma_{DC} \approx s_{AC}^{'} \approx 1$ S/cm at 6.5 GHz [9]. Apparently lower values of $s_{AC}^{'}$ seems to indicate that the studied material is only partially an intrinsic conductor. At low frequencies, the effects of polarization and conduction can be easily separated since instantaneous response between the field and the current leads to a conduction loss that is frequency independent. However, when it takes a certain time for the current to reach its equilibrium value the conductivity becomes complex $s^* = s^i + is^{''}$. The out of phase $s^{''}$ represents a quasi-localized charge displacement that is equivalent to a dipolar process contributing to the dielectric constant $e_r^{'}$. Analysis of the dielectric data on the complex plane shown in Fig. 3 indicates that a dielectric-like relaxation process in ES can be recognized at frequency of about 6.8 GHz. This frequency is lower than the plasma frequency suggested for the charge carriers in a highly metallic polyaniline [2].
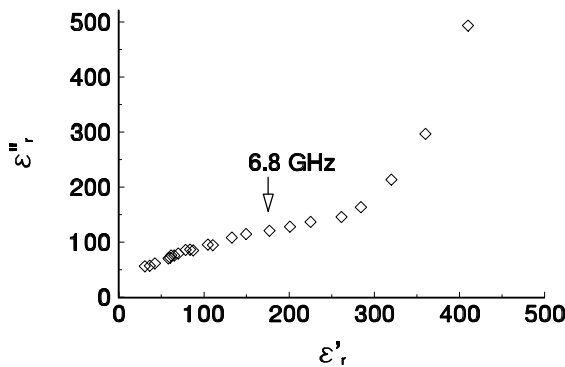
In order to verify whether the observed relaxation is related to the charge transport mechanism or rather to the bound-charge motion within a single domain, we studied dielectric mixing rules for ES composites. A family of dielectric mixing formulas, including the simplest Maxwell Garnet that can be used to determine the nature of the mixing, has been presented in the reference [9]. Low frequency impedance measurements revealed that composites of ES particles with non-conducting epoxy glasses have an on-set percolation threshold at volume fraction of about 16 %. Based on microscopic data and the AC impedance data we concluded that for volume fractions less than 10 % the composites can be described as falling into the category of 3-0 connectivity with ES particles randomly dispersed having connectivity of 0 in the surrounding epoxy matrix having connectivity of 3. At higher volume concentration approaching the percolation threshold, the ES phase forms continuous structures that have connectivity greater than zero. Adding ES to the non-conducting epoxy resin increases the dielectric constant of the composite. However, the resulting dielectric constant is lower than the values inferred from the dielectric mixing rules. For example, at 6 GHz the dielectric constant of the epoxy matrix increases from 2.77 ± 0.06 to 3.0 ± 0.1 for the ES volume

Fig, 3 Dielectric permittivity of ES on the complex plane.

fraction of 9.1 % and to about 3.5± 0.1 for the ES volume fraction of 15.1 %. The 3-0 connectivity model calculates the dielectric constant of the composite to be about 3.56 and 4.16 respectively. Thus the apparent dielectric constant of the ES may be only 6.26 in the 9 % composite. This value increases to about 12.5 in the 15 % composite, but it is far less than the 200 value determined for the 100 % ES. With increasing connectivity, the conducting domains become increasingly coupled, which extends charge transport and increases the associated polarization. Therefore the high value of the microwave dielectric constant can be attributed to a charge transport mechanism in ES. In ES composites in which coupling interaction is interrupted by a non-conducting phase boundary the microwave dielectric polarizability becomes reminiscent of localized states in organic solids.

## CONCLUSION

The electromagnetic properties, permittivity and conductivity, of emeraldine salt and its epoxy resin composites were determined in the microwave frequency range. The observed high value of the microwave dielectric constant is attributed to polarizability originating from a delayed charge transfer between conducting domains with an apparent relaxation at about 6.8 GHz. In composites in which coupling between the conducting domains is weakened by a non-conducting phase boundary, the microwave dielectric polarizability becomes reminiscent of localized states in organic solids.

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