Measurement of the Broadband Microwave Absorption and Shielding Characteristics of a Conductive Polymer

K. Naishadham
Department of Electrical Engineering
Wright State University
Dayton, OH 45435
knaish@cs.wright.edu

P. Chandrasekhar
Ashwin-Ushas Corporation, Inc.
206 Ticonderoga Blvd.
Freehold, NJ 07728
ashwinusha@aol.com

Abstract: Conducting Polymers (CPs), a new class of organic materials displaying high conductivity/weight ratios, have evinced much interest recently in applications involving microwave absorption and EMI shielding. Prior microwave measurements on CPs have been limited to single frequencies or narrow bands, thin films, and permittivity measurements. In this communication, we report the first cumulative broadband measurements and computations of all microwave parameters of a CP relevant for practical application, namely, conductivity, absorption, complex permittivity, shielding and reflection. The specific CP selected is poly(aniline) (P(ANi)) doubly doped with two unique sulfonate dopants. Measurements have been carried out over a 2 to 18 GHz frequency band, on bulk P(ANi), using coaxial line techniques. Comparison with prior results on CPs shows high microwave attenuation for this polymer.

1. Introduction

Conducting Polymers (CPs) are a relatively new class of organic materials displaying as their foremost property a high conductivity combined with very light weight, flexibility and reasonably facile processibility. Due to their high conductivity/weight ratio, they have recently evinced much interest in potential applications as EMI shielding screens, coatings or jackets for flexible conductors, and broadband microwave absorbers [1] – [3]. The absorption characteristic in particular has many military and aerospace applications, including stealth, where conductive composites studied thus far have been relatively poor broadband performers, and where CPs appear to be one of the few materials capable of dynamic (switchable) microwave absorption. Microwave investigations on CPs thus far have been mostly confined to measurements at single frequencies, narrow-band measurements in very limited ranges in a resonant cavity, or measurements mostly of thin films; nearly all have neglected parameters such as absorption, shielding and reflection, which are important determinants of practical application [4] – [11]. In this communication, we report the first cumulative broadband measurements and computations of all microwave parameters of a CP relevant for practical application, namely, conductivity, absorption, complex permittivity, shielding and reflection. The specific CP selected is poly(aniline) (P(ANi)) doubly doped with two sulfonate dopants, which also afford it exceptional environmental durability. Measurements have been carried out over a wide frequency band of 2 to 18 GHz, on bulk P(ANi), using coaxial line techniques. This work supplements our initial work on the CPs, poly(acetylene) (P(Ac)) and poly(p-phenylene-benzobisthiazole) (P(BT)) [12] – [14].

The S-parameters of P(ANi) samples were measured using a precision 7 mm beadless air line on an HP 8510 Vector Network Analyzer (NA). The complex dielectric constant of the sample was determined by computing the roots of a reference–plane independent transcendental equation derived from a transmission line model of the measurement system [15]. Unlike the well-known Nicholson Ross method [16], the Baker-Jarvis method [15] does not break down when the sample thickness becomes an integral multiple of half wavelength in the material, and is robust for lossy samples. Because our samples are smaller than the half wavelength even at 18 GHz, the electrical resonance break–down is not a problem in our case. However, the samples are very lossy, and hence, extreme care has to be exercised in order to prevent small measurement errors from adversely influencing the material properties being measured. This has been achieved by time–gating reflections off the connector transitions, using clean samples, precise calibration at the connector interfaces, and a robust algorithm to solve for the complex roots of the transcendental equation.

In the sequel, we first briefly describe the sample preparation method. Then, we summarize the basic measurement technique and describe the parameter extraction from the measured data. Since the reflection/transmission method using a coaxial line or a waveguide is well–known, no attempt is made to elaborate on the measurement method. It suffices to say that we have chosen this method for two reasons: (a) it is relatively simple and wide–band, (b) since the measurements are taken for the TEM mode of propa-

0-7803-4471-5/98/$10.00 (c) 1998 IEEE

gation, the absorption and transmittivity of the sample are indicative of scaled–down plane wave measurements in an ancheoic chamber. The paper concludes with presentation and discussion of measured dielectric constant, conductivity, absorption and shielding effectiveness (SE).

2. Sample Preparation

P(ANi) exists in several oxidation states with electrical conductivities varying progressively from 10^{-11} S/cm to more than 10 S/cm. It is synthesized by chemical oxidation of aniline in aqueous acidic media, using a common oxidant, such as ammonium peroxydisulfate. In our application, pressed pellets of doped P(ANi), of thickness approximately 4 mm and diameter about half an inch, were produced on a Carver dye press. The disc sample was milled to a cylindrical toroidal shape of inner diameter 0.12 inch and outer diameter 0.269 inch (7 mm) so as to snugly fit in the precision beadless air line. The sample was cleaned thoroughly and examined for mechanical integrity. The DC conductivity of the sample was measured at 11 S/cm using the four–probe technique.

3. Measurement Details

The experimental set–up consists of an HP 8510B Network Analyzer with a sythesized sweep oscillator source and an S-parameter test set. A 10 mm long gold–plated coaxial air line with precision 7 mm connector interfaces is used to hold the annular cylindrical sample. The NA is calibrated for full two–port measurements of reflection and transmission at each port. The air line is connected between the two ports and all the four S-parameters are measured between 2 GHz and 18 GHz, accurately locating and gating out any connector mismatches. Then the sample is introduced into the air line and the complex S-parameters are measured using the time domain gating feature.

A simple, albeit non–linear, transcendental equation can be derived, which relates the four measured S-parameters to the complex permittivity of the sample [15]. Assuming that the material is non–magnetic, the transcendental equation for the complex dielectric constant, ϵ_r, is

$$\frac{S_{11}S_{22}}{S_{21}S_{12}} + \frac{(\epsilon_r - 1)^2}{4\epsilon_r}\sin^2(\beta d) = 0 \tag{1}$$

where d is the thickness of the sample and

$$\beta = \frac{2\pi f}{c}\sqrt{\epsilon_r} \tag{2}$$

with f being the frequency and c the speed of light in air. Eq. (1) is solved for ϵ_r at each frequency using the Davidenko's method. The parametric reduction of measured data to complex permittivity on very lossy samples has been an elusive numerical problem as exemplified by the drawbacks of the Nicholson-Ross method and its variants. Hence, it is in order to describe the specific algorithm that we employ for the purpose, and to subsequently demonstrate its accuracy.

The basic idea of Davidenko's method [17] is to transform a system of non-linear algebraic equations in n unknowns to a set of n first-order ordinary differential equations (ODEs) in a dummy variable t, and then solve the ODEs numerically. The numerical solution of these ODEs is more stable and efficient than root-finding algorithms such as Newton's and Muller's methods, which are prone to instability or convergence to the wrong root if the initial guess is not specified accurately. Davidenko's method is relatively insensitive to the initial guess and converges to the "final" solution exponentially.

Davidenko's method can be simply illustrated as follows. Assume that we have a first-order ODE

$$\frac{df(x)}{dt} = -f(x) \tag{3}$$

where x is a function of t. It is equivalent to

$$\frac{dx}{dt} = -\frac{f(x)}{\frac{df(x)}{dx}}. \tag{4}$$

The solution of eq. (4) is

$$f(x) = ce^{-t} \tag{5}$$

where c is a constant. For $t \rightarrow \infty$, we have

$$f(x) = 0. \tag{6}$$

It implies that the solution of eq. (6) is just the solution of eq. (4) for $t \rightarrow \infty$. So, in principle, by solving eq. (4) for sufficiently large t, we can approximate the solution of eq. (6) as close as we desire. The exponential convergence of the solution is evident from (5).

Using this idea on (1), re–written as

$$F(\epsilon_r) = 0, \qquad \epsilon_r = \alpha + j\beta \tag{7}$$

we obtain the following coupled first-order real ODEs:

$$\frac{d\alpha}{dt} = -\frac{1}{\mid F_\epsilon \mid^2}(Re[F]Re[F_\epsilon] + Im[F]Im[F_\epsilon]) \tag{8}$$

$$\frac{d\beta}{dt} = \frac{1}{\mid F_\epsilon \mid^2}(Re[F]Im[F_\epsilon] - Im[F]Re[F_\epsilon]) \tag{9}$$

where F_ϵ is the (complex) derivative with respect to ϵ. We have solved these ODEs numerically by the Runge-Kutta method, and F_ϵ has been approximated by its central finite difference.

4. Measured Results

In order to test the measurement technique and the parameter extraction algorithm, we first calculated the permittivity of air in an empty coaxial line. The results are shown in Fig. 1. The real part of the dielectric constant is about 1.0015 over the 45 MHz to 18 GHz band, and by a least squares fit to the imaginary part data shown in Fig. 1, the average value of the imaginary part is determined

0-7803-4471-5/98/$10.00 (c) 1998 IEEE

to be about 0.001 over the 2 to 18 GHz band. The worst case uncertainty at 10 GHz is calculated as 0.15%. Good corroboration of the measured complex dielectric constant with the known values has also been observed for reflection/transmission measurements on teflon and nylon. The samples in each case have a nominal thickness of 5 mm.

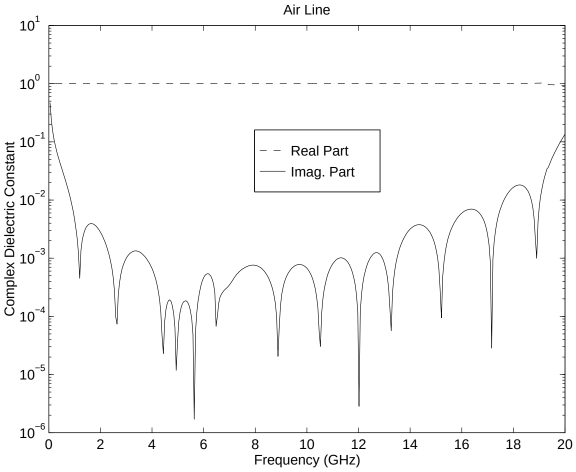

Figure 1: Complex dielectric constant in an empty coaxial APC 7mm air line.

Fig. 2 depicts the measured S-parameters as functions of frequency for a representative P(ANi) sample. The sample was carefully positioned in the middle of the 10 mm air line, and all positions and lengths have been measured by tracking time-delays. It is seen that the difference between S_{11} and S_{22} or between S_{12} and S_{21} is quite small. Most notably, between 11 and 18 GHz, S_{21} becomes very small (about 70 dB).

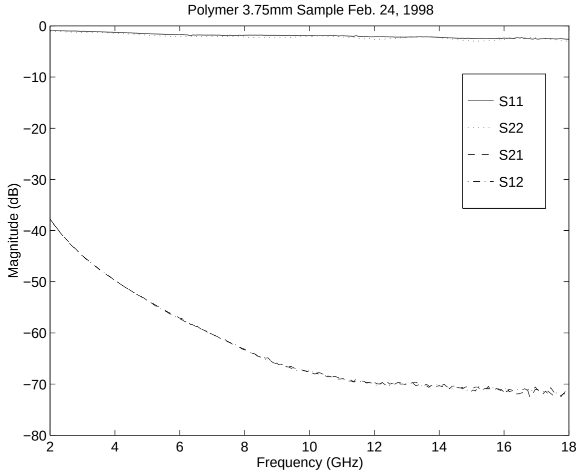

Figure 2: Magnitude of the S-parameters of P(ANi) sample in a coaxial fixture.

The complex permittivity reduced from these S-parameters is plotted in Fig. 3. The real part varies from 180 at 2 GHz to about 1 at 10 GHz. The small oscillation about unity between 10 and 16 GHz is presumably due to the small values of S_{12} and S_{21}. The phase uncertainty on measured S-parameters increases at small magnitudes. The high values of (real) permittivity are characteristic of conductive polymers, and is partially attributed to the disorder on the motion of charge carriers [10]. For comparison, as a function of dopant levels, Javadi et al. [10] measured values ranging from 10 to 120 (room temperature) using a cavity resonant at 6.5 GHz. The permittivity variation in Fig. 3 is also consistent with previous 130 MHz to 20 GHz measurements on P(Ani) doped with naphthalene disulfonic acid [5]. Interestingly, Lafosse [6] measured the permittivity of a poly(pyrrole)–teflon alloy between 10 MHz and 6 GHz, and also found that the permittivity decreases monotonically as a function of frequency, similar to Fig. 3.

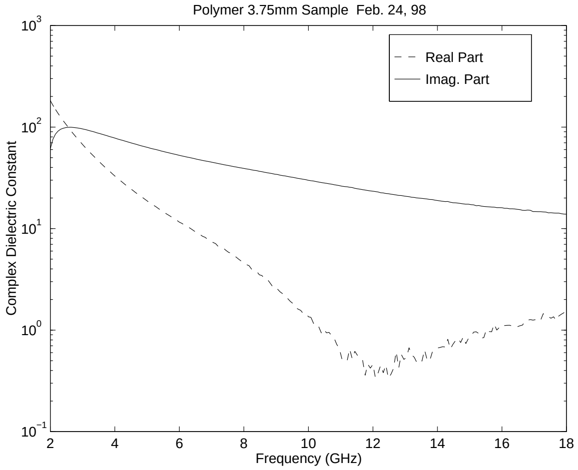

Figure 3: Complex permittivity of the polymer sample.

A better corroboration for CPs is the electrical conductivity, calculated from the imaginary part of the dielectric constant as $\sigma = \omega\epsilon''\epsilon_0$. The conductivity is plotted in Fig. 4, and varies between about 18 S/cm at 4 GHz and 14 S/cm at 18 GHz. The nominal measured DC conductivity for the material is about 11 S/cm, in reasonable agreement with the data in Fig. 4. For comparison, the highest room temperature conductivity reported in [10] at 6.5 GHz is about an order of magnitude smaller than the value in Fig. 4.

The microwave shielding effectiveness of the polymer calculated from the transmission coefficient of the sample [13] using the measured complex permittivity, is plotted in Fig. 5. The SE is lower than -25 dB over most of the band. In particular, in the X and K radar bands, the SE is lower than -32 dB. Better values can be obtained by stacking several polymeric sheets of different thicknesses, or by sandwiching a lossy dielectric between two sheets of the same thickness [13]. The return or reflection loss can also be computed from the measured reflection coefficient, corrected for the

0-7803-4471-5/98/$10.00 (c) 1998 IEEE

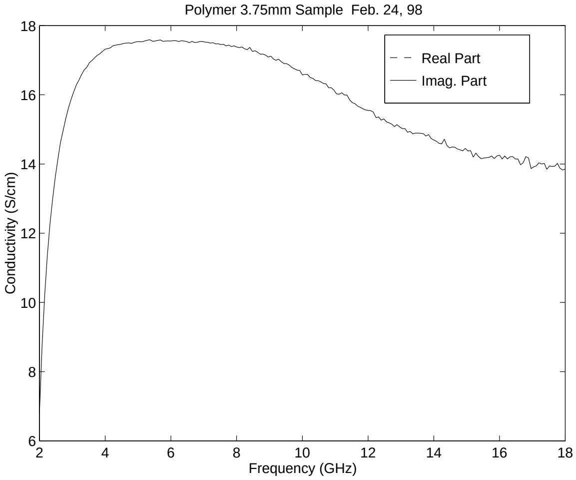

Figure 4: Conductivity of the polymer sample.

losses in the transmission line. Fig. 5 shows nominal return loss of -3 to -1 dB. The microwave absorption in the sample, calculated as $[1- \mid S_{11} \mid^2 - \mid S_{21} \mid^2]$ expressed in dB (with the S-parameter values at the sample face), is also depicted in Fig. 5. Interestingly, in the X and K bands, the nominal absorption is about -5 dB, and can be improved by using multilayered screens [12].

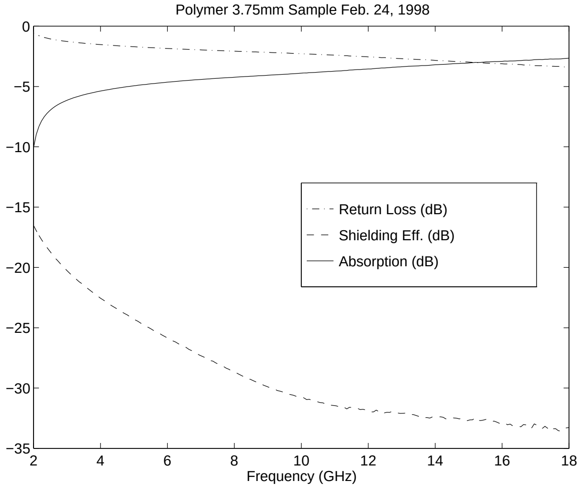

Figure 5: Shielding effectiveness, reflection loss and microwave absorption of the polymer sample.

5. Summary

We have measured the microwave conductivity, reflection, absorption and shielding effectiveness of bulk samples of P(ANi) doubly doped with unique sulfonate dopants, in a wide frequency range encompassing the X and K radar bands. In contrast to prior microwave measurements on CPs, these represent the first broadband measurements of all parameters of interest for practical application as radar absorbers or EMI shielding materials. A robust algorithm has been employed to extract the material parameters from the measured data. We are currently pursuing more detailed studies involving the influence of varied dopants and doping levels.

References

[1] T.A. Skotheim, R.L. Elsenbaumer and J.R. Reynolds (Eds.), *Handbook of Conducting Polymers*, Second Edition, Marcel Dekker, Inc., New York, (1997).

[2] H.S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers* (four volumes), John Wiley, New York, (1997).

[3] P. Chandrasekhar, *Conducting Polymers: Fundamentals and Applications, A Practical Approach*, Kluwer Academic Publishers, 1998 (in press).

[4] P. Hourquebie, L. Olmedo and C. Deleuze, in H. Kuzmani, M. Mehring and S. Roth, (Eds.), Springer Series in Solid-State Sciences, **107** (*Electronic Properties of Polymers*), 125 (1992).

[5] L. Olmedo, P. Hourquebie, and F. Jousse, *Synth. Met.*, **69**, 205, (1995).

[6] X. Lafosse, *Synth. Met.*, **68**, 227 (1995).

[7] L.J. Buckley and M. Eashoo, *Synth. Met.*, **78**, 1, (1996).

[8] H.S. Lee, E.S. Choi, E.B. Park, J.Y. Park, Y.W. Park, C.S. Hwang and T.W. Kim, *Synth. Met.*, **69**, 75 (1995).

[9] Z.H. Wang, E.M. Scherr, A.G. MacDiarmid and A.J. Epstein, *Phys. Rev. B*, **45** (8), 4190 (1992).

[10] H.H.S. Javadi, K.R. Cromack, A.G. MacDiarmid and A.J. Epstein, *Phys. Rev. B*, **39** (6), 3579 (1989).

[11] H. Naarman, *Proc. Int. Congress of Synthetic Metals*, Paper No. 4A-07, 1986.

[12] K. Naishadham and P.K. Kadaba, *IEEE Trans. Microwave Theory Tech.*, **MTT-39** (7), 1158, (1991).

[13] K. Naishadham, *IEEE Trans. Electromag. Compat.*, **EMC-34** (1), 47, (1992).

[14] K. Naishadham, *Proc. 7th International SAMPE Electronics Conf.*, 252 (1994).

[15] J. Baker-Jarvis, E.J. Vanzura, and W.A. Kissick, *IEEE Trans. Microwave Theory Tech.*, **MTT-38** (8), 1096, (1990).

[16] A.M. Nicolson and G.F. Ross, *IEEE Trans. Instrum. Meas.*, **IM-17**, 395, (1968).

[17] K. Naishadham and L.B. Felsen, *IEEE Trans. Antennas Propagat.*, **AP-41** (3), 304, (1993).

0-7803-4471-5/98/$10.00 (c) 1998 IEEE