# Conducting dielectric polymer properties at Terahertz wavelength

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**Abstract**: The dielectric function of polyaniline (Pani) doped by couple drug/solvent sulphonic camphoracid/dichloroacetic CSA/DCAA is studied in the terahertz range. Numerous films of this polymer with different doping level are measured by Terahertz Time-Domain Spectroscopy (THz-TDS). The Fourier transmission spectrum, the permittivity and conductivity are then precisely obtained between 0.1 and 4 THz. The behavior of the dielectric function does not follow Drude theory and the extracted data are well fitted and analysed by Jonscher's universal dielectric response. Furthermore, we will present experimental results of shielding effectiveness (SE) obtained at high frequency from several polyaniline films.

Among conducting plastics polyaniline stands out due to its outstanding properties. It is one of the so-called doped polymers, in which conductivity results from a process of partial oxidation or reduction. Polyaniline compounds can be designed to achieve the required conductivity for a given application. The resultant blends can be as conductive as silicon and germanium or as insulating as glass. Another advantage is that it is both melt and solution processable. This means that the compound can be easily mixed with conventional polymers and that it is easy to fabricate polyaniline products into required shapes.

An increase and the control of electrical conductivity in these polymers become a priority research orientation making credible the industrial development of these materials**.** It is accordingly that the synthesis of a conducting composite containing polyaniline was carried out. Experiments, in low frequency range were carried out in order to study the movement of the free charge in conducting polymers, provided information on static conductivity[1-2]. The static conductivity of the polyaniline was well studied, what is not the case of dynamic conductivity in low frequency [3] because the spectra are very narrow and thus not easily exploitable. However, to clearly foresee the potential industrial developments of these compounds, it is necessary to qualitatively and quantitatively characterize the optical and dielectric properties.

In this situation, non-invasive methods such as optical and spectroscopic techniques at very high frequency are of particular interest, especially in the far infrared where collective behaviors are revealed. In this letter, we present measurements of permittivity and conductivity obtained at room temperature for the polyaniline (Pani) doped by the couple doping-solvent sulphonic camphoracid /dichloroacetic (CSA/DCAA) and to supply experimental data at Terahertz wavelengths. In this work, we present measurements of permittivity and conductivity obtained at room temperature for composites polyaniline (PANI)-CSA/Polyurethane and we measure the dielectric behavior at Terahertz wavelengths by terahertz time domain spectroscopy (THz TDS). The variation of the complex dielectric function is analyzed by a frequency dependence proposed by Mott and Davis[4]. The percolation threshold in the submillimeter range is deduced from comparative measurements of different samples which differ by their doping level.

**Technique:** Our femtosecond THz pulse spectrometer consists of a Kerr-lens mode-locked Ti: sapphire laser yielding 80 fs pulses at 76 MHz repetition rate. The output pulse train is split into pump and probe beams. These two optical pulses are focused onto photoconductive antennas fabricated on low temperature grown GaAs. These ultra speed optical switches are used for the generation and the detection of the THz beams. After collimation with off axis parabolic mirrors, the THz beam is focused within the sample and the transmitted beam is measured by photoconductive sampling. The beam diameter cross section is estimated to be 2 mm at the focus. The current induced by the probe beam in the coherent detector is amplified and processed with a lock-in digital amplifier (Stanford SRS 830) referenced by a mechanical chopper. This combination of our setup has a frequency response up to 2.5 THz and in this work, with a surface field emitter, we reach 4 THz bandwidth. [5-6].

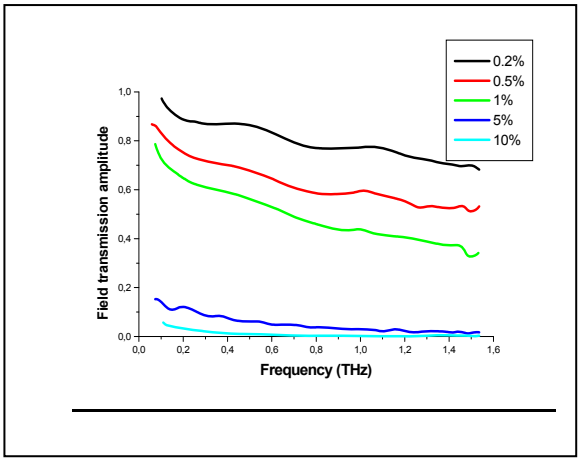


**Fig 1 Transfer function of conducting polymer**

Our sample is polyaniline which is a conducting polymer pertaining to family of semi flexible polymers and it exists in several forms according to the oxidation step. The form Emeraldine-Bases (Pani-EB) was selected for its strong stability with ambient temperature and best results of electric conductivity. The couple drug/solvent having the best result in term of conductivity is the couple sulphonic camphor acid/dichloroacetic (CSA/DCAA). In parallel, the polyurethane (PU) is an elastic thermoplastic, flexible device also being used as heat insulator. The dissolution of the DCAA in its centre makes it possible to obtain a homogeneous solution meeting the same characteristics as the Polyurethane. The solvent being dissolves in the Polyurethane (PU), consequently we will name our composites Pani-CSA/PU. The doping of CSA/DCAA in Pani-EB was carried out by protonation because it is easy to implement and present good output in term of conductivity. Five samples with levels of different doping (0.2%; 0.5%; 1%; 5%; and 10%) were characterized by THz-TDS. We limited our study on samples having doping level up to 10% because for higher concentration, the transmitted signals are too low and data are not exploitable.

Figure 1 shows a series of FFT amplitude of the transfer function obtained for different doping levels. Since each polymer has its own thickness measured with 1% precision, time shift of data with respect of the reference signal is relative to the optical thickness. Typically the sample thickness is ranging from 100 to 185 µm.

For the interpretation of extracted data, it has been classical to present results in term of $\varepsilon'(\omega)$ the real part of the permittivity function and $\sigma(\omega)$ where $\sigma(\omega)$ is the real part of the conductivity and related to the dielectric loss by $\sigma(\omega) = \varepsilon_o\omega\varepsilon''(\omega)$, where $\omega=2\pi f$, f being the measuring frequency available in our experiment, and $\varepsilon_o$ the free space permittivity. In this work, we have used these parameters for the presentation of the results. We show in figure 2 the variation of the total conductivity as a function of frequency in the THz range. We observe an awaited strong evolution of the conductivity as a function of the doping level but also a smooth variation with the frequency. This behavior can be well described by the frequency dependence of the form given by Mott and Davies [6]

$$\sigma(\omega)=A\omega^s \quad (1)$$

Where s is a parameter less than unity and decreases with the doping level. We found s ~ 0.6 for low doping level ( i.e.< 1% ) and s~0.22 for higher concentrations. Since, there are some free charges which give rise to DC conductivity without giving any contribution to the dielectric polarization; we compared results obtained by static conductivity given by the four points technique and the results of dynamic conductivity given by the spectroscopy terahertz at 0,2THz. Good agreements are found at room temperature suggesting the difficulty to extract quantitatively the static part of the conductivity with respect to the dynamic one. For the dielectric analysis, the absence of well defined $\varepsilon''(\omega)$ peak are attributed to mixed conduction effects. Quantum mechanical effects of electron through a barrier, hopping of electrons over a barrier are probably dominant mechanism of the dielectric behaviour. In a polaron system where the relaxation frequency time strongly depends on temperature, the charge carriers are trapped at impurity defects and hopping conduction lead to dielectric relaxation. However, the optical conductivity of this polymer, like most correlated metals, drops off as power of the frequency that is much smaller than two. When these power law conductivities are measured in the infrared frequency regime above the THz regime, such measurements led to the speculation that the Drude power

laws could not be used for the description of the dielectric behaviour. Moreover, no clear Debye-type loss peak is observed by subtracting the contribution of $\sigma_{dc}$ from $\sigma(\omega)_m$ in all the bandwidth under investigation and in all the microwave measurements. This behaviour is consistent with carrier-dominated systems in which charges make the dominant contribution to polarization [7]. In this system, we propose to characterize this low-frequency dispersion system by Jonscher's universal law with exponent typically in the range $0.5<n<0.9$, which means a much lower loss and a flatter frequency dependence [7].

Moreover, the threshold of percolation of our samples is found at 0.18% from DC measurements and consequently we observe an important increase in real terahertz conductivity between films of concentration 0.2% and films concentration 0.5%.

At least, we extracted from the conductivity values, the skin depth and the shielding effectiveness (SE) obtained by our measurements for all samples in the entire bandwidth available. The theoretical results of the SE are in good agreement with our experimental results. The improvement of SE mainly depends on the conductivity level and thickness of polyaniline and is correlated to physical mechanism involved in the frequency dependence of the conductivity. It is necessary to manufacture highly conducting materials with a low thickness because material lightness is a paramount criterion in the choice of materials being used as electromagnetic screens. For example, these films can be specifically selected in the sight of an objective laid down in electromagnetic terms of electromagnetic compatibility. With a mono layer structure of polyaniline film 10% we measured values of 40 dB in terms of shielding effectiveness in the submillimetre wavelength.

**In conclusion**, we have shown that the THz-TDs technique can be efficiently used to quantitatively characterize the far infrared dielectric properties of polyaniline (Pani) doped by couple drug/solvent sulphonic camphoracid/dichloroacetic CSA/DCAA compounds. Permittivity and conductivity dispersion are found to be in good agreement with polaron description model. We also estimate the percolation threshold and the shielding effectiveness of this doped polymer in the sub mm range.

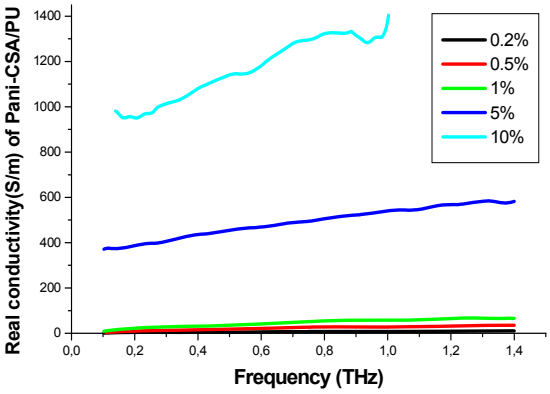


Figure 2 conductivity of 0.2%; 0.5% ; 1% ; 5% and 10% measured by THz-TDS

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