

Frequency And Temperature Effects On Dielectric Properties Of PEDOT-VC Copolymer

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Keywords: Conjugated Copolymer, Dielectric Spectroscopy, Permittivity, Conductivity.

Abstract: The copolymer based on Poly(3,4-Ethylene dioxythiophen) and Poly(n-Vinylcarbazole) was characterized by FTIR and Raman spectroscopy. The temperature and frequency evolutions of dielectric parameters are also plotted and studied. The dependence of ϵ'' on the temperature shows relaxation process for studied copolymer especially with frequencies about 1kHz for the temperatures: $90^{\circ}\text{C} < T < 118^{\circ}\text{C}$. The values of ϵ'_{∞} , ϵ''_{MAX} , relaxation time and DC conductivity corresponding to the copolymer are also determined with the aim to provide dielectric analysis involving vital information about this new polymeric compound.

1 INTRODUCTION

For decades, the plastic electronic or flexible electronic has evoked considerable interest. It is developed by young process such as: Roll-to-Roll and inkjet printing routes [1-3]. Many conjugated polymer are aimed at being deposited in devices with flexible substrates [4], so they have the advantage of being included by easy process. These materials are widely studied as organic semi-conducting materials [5-9]. Thanks to their low cost [10-12], an enormous number of applications have been found for these compounds in industry like to solar cells [13], field effect transistors [14], optical and display devices [15], electronic memories [16] and supercapacitor electrodes [17]. Since the Shirakawa Polyacetylene [18], much work has been carried out to construct organic compounds with functionalized properties including the low band gap energy and high conductivity [19]. However, little attention has been paid to the dielectric behaviour of this class of materials.

The knowledge of the electric parameters presents a direct practical importance. Basically, materials showing good characteristics such as high dielectric constant, low dielectric loss and good thermal stability, are the well-developed microwave device compounds destined for resonators, phase shifters

and tunable mixers [20]. In molecular designing, the addition of appropriate functional group could lead to new properties, even to a many prospects [21]. Thus, we aim to present an experimental study on the (PEDOT-VC) which constitutes copolymer (Figure.1) based on assembly of two segments EDOT and VC: the Poly (3,4-Ethylene Di-Oxy-Thiophen) with Poly (n-Vinyl-Carbazole) [22].

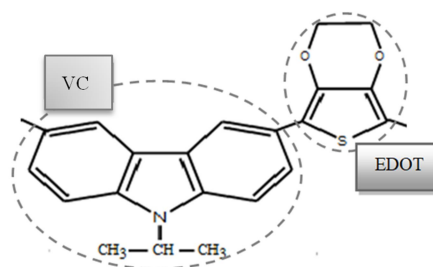


Figure 1: Chemical Structure of EDOT-VC monomer.

The family of PVC is attractive for optoelectronics, Since the late fifties, the interest in these polymers began especially with Rosenberg's work on electrophotographic applications [23], and later IBM uses PVC / (2,4,7) Tri-nitrofluorene for the first time as an organic photoconductor [24]. In addition, PEDOT is a transparent and thermally stable conductive polymer. It constitutes the subject of a large number of publications in the area of Bulk

Heterojunction (BHJ) Solar Cells [25]. To improve its solubility, it is often found as composite with PolySulfonate-Styrene (PEDOT:PSS). In Bulk Heterojunction, PEDOT acts as an electron donor material, where fullerene derivatives C60 represent the acceptor. It is also possible to use it as a buffer layer situated between the anode and the active layer of a solar cell. So, during the photogeneration the impurities diffusion between anode and organic layer is limited, which improves the performance of the cell.

In this paper, we depict firstly the characterization of PEDOT-VC by FTIR and Raman techniques. The dielectric studies were achieved upon pressed pellet. Therefore, our main is to study the dielectric behaviour as well as to understand the conduction mechanism for this new copolymer.

2 CHARACTERIZATION

In this work, the copolymer is characterized chemically using spectroscopic methods: Infrared and Ra-man. FTIR study was carried out over mid-infrared in the range of 4000 cm^{-1} to 400 cm^{-1} , and 16 scans were taken with spectral resolution of 4 cm^{-1} . For the Raman scan a spectrometer Senterra was used, the exciting radiation was 785 nm , laser power at 1 mW , with CCD-Detector cooled until $T=204\text{K}$. Analysis was performed in the region of 3000 cm^{-1} to 200 cm^{-1} , with attenuated fluorescence effect. The dielectric measurements were performed within the temperature comprised between 25°C and -120°C using programmable four with probe. The frequency analysis was carried out using computerized LCR-meter (Agilent E4980A) in large frequency range 20Hz to 2 MHz with excitation of 1 Volt . PEDOT-VC pellet sandwiched between two copper electrodes was silver-lacquered to obtain better contact.

3 RESULTS AND DISCUSSION:

3.1 FTIR Analysis:

For a structural characterization of the copolymer by FTIR spectroscopy (Figure 2), several characteristic bands are identified: around 511 cm^{-1} the modes are assigned to the shear and wagg of the CH_3 groups, the band observed at 830 cm^{-1} is due to deformation outside the plane of the C-H Thiophen rings. Also the band at 1040 cm^{-1} is attributed to the C-O stretching, the vibration related to the C-N

stretching of Carbazole is in the region of 1185 cm^{-1} , and C-H shear mode of Vinyl group on 1350 cm^{-1} .

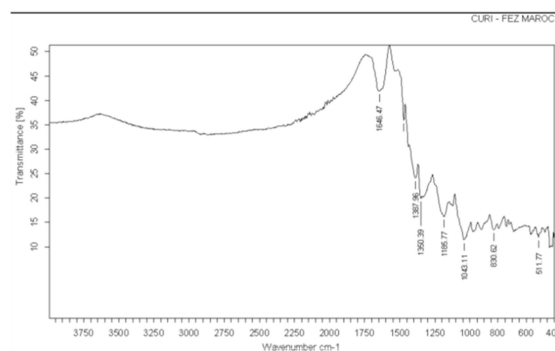


Figure 2: FTIR spectra of PEDOT-VC

3.2 Raman Analysis:

The structural analysis carried out by FTIR was supplemented by Raman spectroscopy. It is showed in Figure 3. The lines obtained are mainly related to the polymeric structure of the PEDOT (Table1).

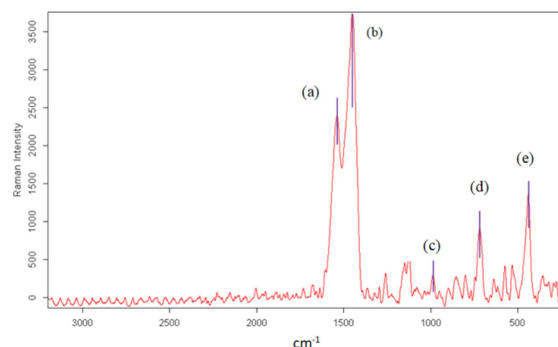


Figure 3: Raman spectra of PEDOT-VC

Table 1: Raman frequencies with relative assignments

$\nu\text{ (cm}^{-1}\text{)}$	Band	Assignment
1563	C = C	asymmetric stretching
1370	C-C	intercyclic stretching
993	C-O-C	cyclic deformation
696	C-S-C	symmetrical deformation
441	C-O-C	deformation

3.3 Dielectric measurements:

PEDOT-VC pellet is considered like planar capacitor. The order of magnitude of obtained capacitance is between 10^{-11} F and 10^{-8} F . The frequency dependences of the real part ϵ' of the studied copolymer are shown in Figure 4, it reports

the experiment dielectric constant required for tree temperatures : at ambient and at elevated temperatures. Theoretically, the complex permittivity can be expressed by different formulas; it refers to the polarization kind. As already noted, in the case of static field ($f \rightarrow 0$) the polarization follows the alternative field, the dielectric constant is maximal for low frequencies, also in optical frequencies ($f \rightarrow \infty$) its value will fall to ϵ_{∞} .

In figure 4, it is clear that in the decreasing order of frequencies, the real permittivity ϵ' of PEDOT-VC rises most rapidly for high temperatures, otherwise it tends to take the same constant value ϵ_{∞} for high frequencies and at different temperatures. This behavior indicates that mechanism governing in PEDOT-VC is near to Debye relaxation [26-27].

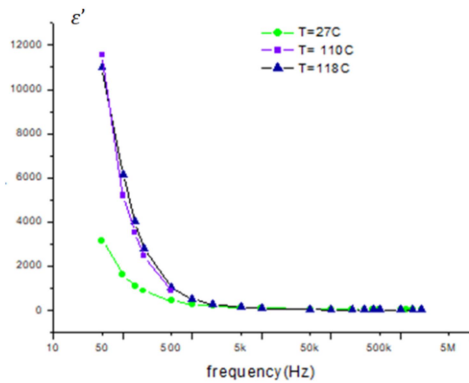


Figure 4: Variation of the real part permittivity ϵ' with the logarithmic frequency scale

The Figure 5 shows the variation of the imaginary permittivity ϵ'' against temperature T for several frequencies. As already noted, the ϵ'' permittivity parameter corresponds to the resistive quality of the material, which is traduced by the dielectric heating. So, a characteristic point is found on ϵ'' evolution across frequency scale that when the loss factor takes generally maximum value. Following Debye relaxation model, the corresponding dielectric relaxation time can be expressed in terms of characteristic frequency:

$$\tau = \frac{1}{2\pi f_c} \quad (1)$$

On the Table 2, the characteristic parameters reflecting the relaxation phenomena have been reported. The obtained value of ϵ'_{∞} is superior of 15, exhibiting high permittivity in comparison with others polymers or inorganic materials cited in literature [28-29]. On other hand, ϵ''_{max} , f_c and τ values are of the same magnitude as the values

found in Polyurethane/Polyaniline composites investigation [30].

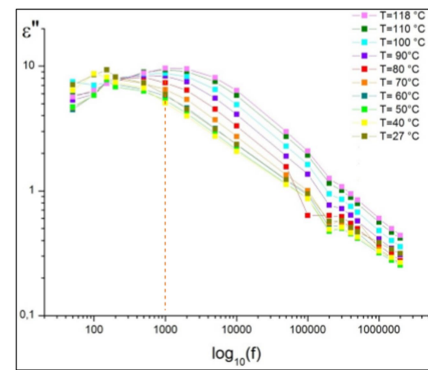


Figure 5: Variation of the imaginary part permittivity ϵ'' with the logarithmic frequency scale

Table 2: Characteristic Parameters of the Relaxation Phenomena

Temperature	ϵ'_{∞}	ϵ''_{max}	f_c (Hz)	τ (μ s)
27 °C	21.75	9.31	-	-
110 °C	17.5	9.36	1000	159.15
118 °C	17.51	9.63	1000	159.15

The figure 6 reproduces the absolute conductivity depending on frequency at ambient temperature. The σ_{abs} values were obtained from the both terms of σ^* complex conductivity: σ'_a real and σ'' imaginary part. In summary, the σ_{abs} conductivity shows an increasing at high frequencies, the frequency dependence of the AC conductivity is likely due to the carrier hops between the states localized in the band gap. The DC conductivity was also determined from the slope of this curve ($\sigma_{DC} \approx 1,37 \cdot 10^{-4}$ S/m).

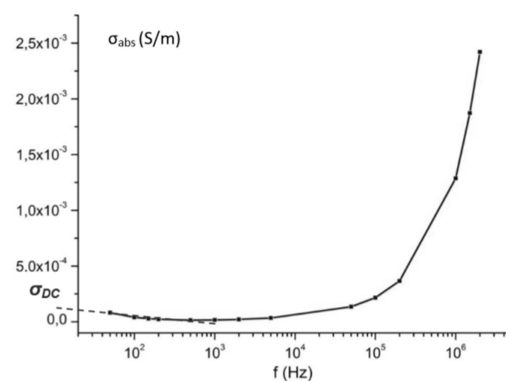


Figure 6: Variation with frequency of absolute conductivity.

We extrapolate activation energy of conductivity from Arrhenius plots [31], the values are calculated

from the slope of the linear fit to the conductivity data. The corresponding activation energy values versus frequency scale are given in figure 7. The copolymer exhibits low energy levels between 0,38eV and 0,54eV for studied frequencies.

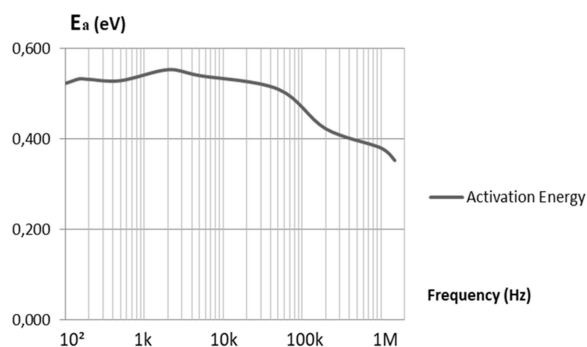


Figure 7: Variation with frequency of the copolymer conductivity.

4 CONCLUSION:

This experimental investigation provides spectroscopic and dielectric analysis for the PEDOT-VK copolymer with the aim to predict functionalized properties of this new polymeric compound. In the present paper, FTIR and Raman spectra of the PEDOT-VK copolymer are recorded and examined. For the frequency study, Debye relaxation process is observed for frequencies around 1kHz within the range $90^{\circ}\text{C} < T < 118^{\circ}\text{C}$. The effect of the temperature, on the both real and imaginary permittivities, was studied corresponding to frequencies ranging from 50 Hz to 2 MHz. Several characteristic parameters related to the dielectric relaxation phenomena have been determined as well. Dielectric and curves data versus the logarithmic frequency scale suggest that charge carrier mechanism could be governed by the hopping model.

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