# Electrical Properties of Poly-N-Epoxypropylcarbazole/Vanadium Pentoxide Composite

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## Abstract

In the present work the electrical properties of poly-N-epoxypropylcarbazole (PEPC) and vanadium pentoxide ($V_2O_5$) composite have been studied. The composite was formed by mixing of PEPC solution in benzene with $V_2O_5$ powder and stirring at room temperature. The composite solution was deposited on a dielectric substrate with copper electrodes and the Cu/PEPC-$V_2O_5$/Cu surface type film samples were fabricated. The Cu/$V_2O_5$/Cu samples were used as a reference where the films were deposited from the mixture of $V_2O_5$ powder in distilled water. Resistance-temperature relationship and voltage-current characteristics of the composite and $V_2O_5$ samples were studied by using conventional digital voltmeter and ammeter in the temperature range of 27-110°C with an error of ±0.5%. It was observed that the DC electrical conductivity, activation energy and non-linearity of voltage-current characteristics of the samples are temperature dependent. It was found that the temperature dependence of electrical conductivity of the $V_2O_5$ samples on the whole obeys $T^{-1/4}$ law whereas the PEPC-$V_2O_5$ ones show visible deviations from that. The PEPC-$V_2O_5$ samples may be used as thermistors as the temperature coefficient of their resistance is large and at 27°C is equal to -4.7%/°C.

## Introduction

As is known, organic materials provide the opportunity to fabricate potentially inexpensive, flexible and light weight, electronic and opto-electronic devices. There has been considerable interest in investigation of organic-inorganic structures: complexes and composites through novel synthesis and self-assembly techniques [1-6]. Investigation of *I-V* characteristics of CdS/polyaniline hetero-junction [1], n-Si/poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) [2] showed rectification behavior, that in the later case read $5.7\times10^5$, that is one of the highest value reported during the last years. Photovoltaic conversion efficiency of 1.11% was measured on NiPc/p-Si hetero-junction [3]. A low switching voltage (2 and 4 V) was observed in organic-inorganic hetero-junction memory element consisting of polyethylene dioxythiophene/polysterene sulfonic acid [4]. The organic semiconductors may be found suitable for applications in many fields of electronics depending on their electrical conductivity [7,8] and very often it determines the characteristics of the devices. For example, the efficiency of an organic solar cells is generally limited due to the low conductivity of photosensitive materials [9,10]. This investigation deals with organic semiconductor such as poly-N-epoxypropylcarbazole (PEPC) that has a potential for applications in electronic engineering. It is known that the structure and properties of organic semiconductors highly depend on their processing technology [7,8]. Generally, the organic materials have large molecular weight, strong intramolecular and weak Van der Waal's intermolecular bonding. The poly-N-epoxypropylcarbazole films grown from solution during rapid stirring [11] showed higher con-

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ductivity than that of the reference samples. In [12] the electrical conductivity of films, composed of two photosensitive organic semiconductors poly-N-epoxipropylcarbazole and copper phthalocyanine deposited from solution at different gravity conditions from 1 g to 1107 g, was investigated. In this work 1.5-fold increase in the conductivity and 2-fold decrease in the activation energy with increased acceleration were reported. A deposition of copper phthalocyanine organic thin films in high gravity by physical vapor transport was studied in [13]. It was shown that the optical absorption increased with increasing acceleration during the film growth. Moreover, the absorption peaks were shifted to lower wavelength values as the acceleration was increased. X-ray diffraction indicated that the centrifugal force caused a strain in the films.

It is generally understood that the fabrication process of organic semiconductor devices is simple, inexpensive and the area may be promising especially for different kinds of sensors design. Electric properties of some organic films deposited at high gravity were explained by space-charge limited currents (SCLC) [14]. Poly-N-epoxipropylcarbazole-copper phthalocyanine films showed highly non-linear voltage-current characteristics. For practical utilization of semiconductor organic thin films it would be important to investigate their electrical properties with different metals (as electrodes) in order to identify whether they form ohmic or Schottky contacts. PEPC as a donor of electrons forms charge-transfer complexes with a number of organic materials that have potential applications in electronic engineering, for example, as a photosensitive material in electro-photography [15].

Vanadium pentoxide ($V_2O_5$) is a well known material. Its composites with polymers, as poly(ethylene oxide)/$V_2O_5$ intercalative nanocomposites [6], and complexes with inorganic oxides as $(V_2O_5)_{1-x}$-$(MoO_3)_x$ [16] have been investigated. These materials, in principle, can posses electrical, optical, and mechanical properties which may not be achieved with each component separately and are interesting for various scientific and technological applications.

In this article, the electrical properties of poly-N-epoxypropylcarbazole and vanadium pentoxide composite were evaluated.

## Experimental

The synthesis of the poly-N-epoxypropylcarbazole is described in details in [15,16]. Polymerization of PEPC was carried out in tetrahydrofuran solution of epoxypropylcarbozole in the pressure of sodium-naphthalene complex (SNC). In the process of polymerization the solution's color is changed from dark green to colorless. It was found that the yield of polymer increases with polymerization temperature ($T = 40$-$50°C$) and concentration ($C = 6.1\times10^{-3}\div1.2\times10^{-1}$ mol/l) of initiator (SNC). The polymerization was conducted in the interval from 8 hrs to 336 hrs. The molecular weight of PEPC was in the range of 707-1493 Da.

The synthesized PEPC was characterized by gel permeation chromatography, electron paramagnetic resonance, infrared spectroscopy and nuclear magnetic resonance [16]. Figure 1 shows a molecular structure of PEPC, where $n$ is about 4-6. The molecular weight of PEPC used by us was equal to 1000 Da. Pure vanadium pentoxide ($V_2O_5$) powder was purchased from the market. As PEPC is dissolved in benzene well and has good adhesion to different substrates [15,16], the composite was formed by mixing 3 wt.% of PEPC powder and 40 wt.% of $V_2O_5$ powder in benzene and stirring at room temperature. The composite solution was deposited on copper electrodes fixed on dielectric substrate and the Cu/PEPC-$V_2O_5$/Cu surface type film samples were fabricated (Fig. 2). As a reference the Cu/$V_2O_5$/Cu samples were used where the films were deposited from a mixture of 40 wt.% of $V_2O_5$ powder in distilled water. The gap between copper electrodes and width of the electrodes were measured by optical microscope and were equal to 0.1 mm and 5-10 mm, respectively. The thickness of the films estimated by SEM was equal to 50-100 μm.

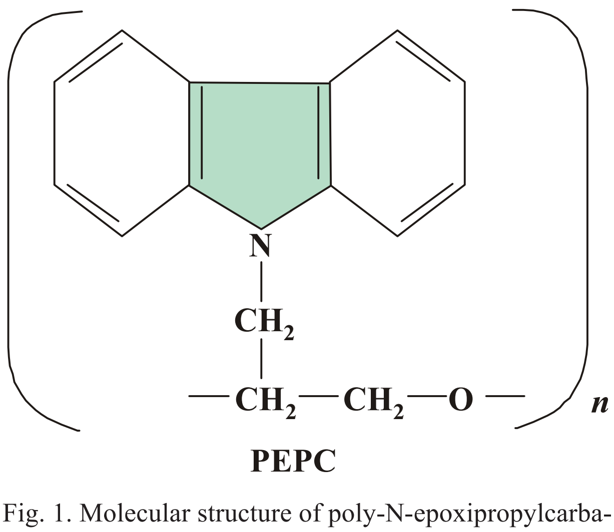


Fig. 1. Molecular structure of poly-N-epoxipropylcarbazole (PEPC).

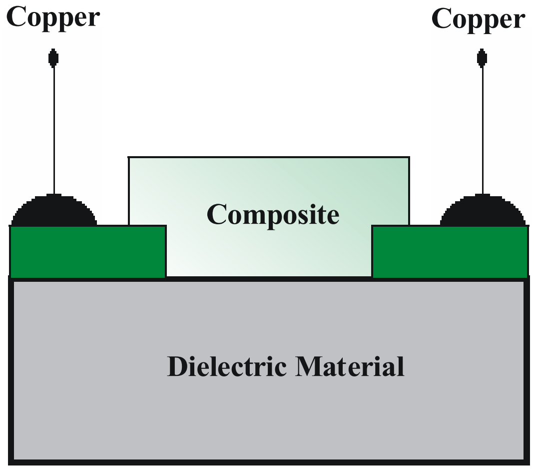


Fig. 2. Cross-section view of the surface type Cu/PEPC-$V_2O_5$/Cu or Cu/$V_2O_5$/Cu samples.

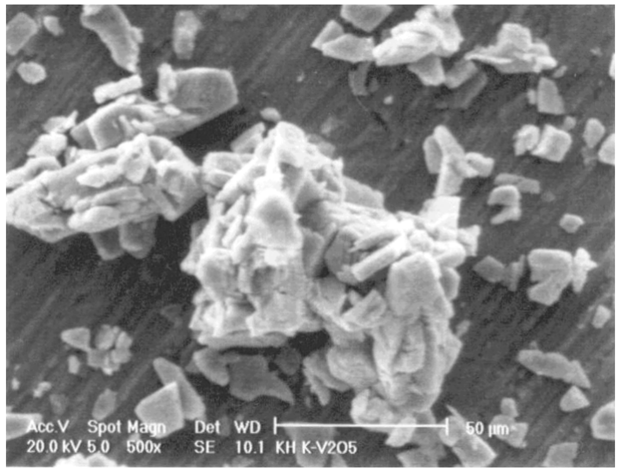


Fig. 3. SEM image of the PEPC-$V_2O_5$ composite film.

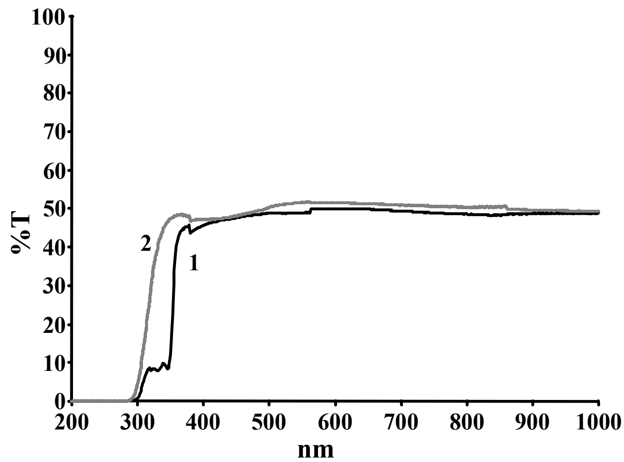


Fig. 4. Wavelength dependence of the optical transmission spectra of the PEPC-$V_2O_5$ (1) and $V_2O_5$ (2) films.

The optical properties were studied on the films deposited on glass substrates by spin coating in the wavelength range of 200-1500 nm using Perkin Elmer (Lambda-19) double beam photo spectrometer. The samples were examined by Philips XL40 scanning electron microscope (SEM).

Resistance-temperature relationships and voltage-current characteristics of the composite and $V_2O_5$ samples were measured by using conventional digital voltmeter and ammeter (HIOKI-3256 Digital Hi Tester) in the temperature range of 27-110°C with an error of ±0.5%.

## Results and Discussion

Figure 3 shows the SEM image of the PECE-$V_2O_5$ composite film. It is seen that the $V_2O_5$ particles (average size was equal to 15 nm) are incorporated in PEPC matrix. Figure 4 shows the wavelength dependence of the optical transmission spectra of the PEPC-$V_2O_5$ (1) and $V_2O_5$ (2) films deposited on glass substrate in the range of 300-1000 nm. The PEPC-$V_2O_5$ and $V_2O_5$ films spectra in principle are like the spectra obtained on the $V_2O_5$ films deposited by electron beam evaporation technique [17] that were blown from a small amount of semi molten material [18]. They have transparency in very wide spectral range. Similarity of the PEPC-$V_2O_5$ composite and $V_2O_5$ transmission spectra shows that complex forming processes were not take place in the composite.

The room temperature conductivities of the composite and $V_2O_5$ were equal to $5\times10^{-8}\ \Omega^{-1}\cdot cm^{-1}$ and $3\times10^{-7}\ \Omega^{-1}\cdot cm^{-1}$, respectively. Figure 5 shows the conductivity-temperature relationship for the Cu/PEPC-$V_2O_5$/Cu and Cu/$V_2O_5$/Cu samples. It is seen that the conductivity increases with temperature. The activation energy ($E$) was determined from the following well-known expression for the conductivity of organic semiconductors as reported in [7,8]:

$$\sigma = \sigma_o \cdot exp(-E/kT) \quad (1)$$

where $k$ is Boltzmann constant, $T$ is absolute temperature and $\sigma_o$ is pre-exponential factor. Room temperature activation energies for the composite and $V_2O_5$ were equal to 0.25 eV and 0.15 eV, respectively. Figure 6 shows the dependence of activation energies on temperature: the relationship shows its complex nature. In [17] it was found that the electrical conductivity behavior of $(V_2O_5)_{1-x}$-$(MoO_3)_x$ thin films obeys the $T^{-1/4}$ law and it was explained by the temperature dependence of individual transition rates, assisted by multiphonon interactions. Figure 7 shows the plots of log$\sigma$ *vs.* $T^{-1/4}$ for the composite and $V_2O_5$, respectively. It is seen that the electrical conductivity of the $V_2O_5$ samples on the whole obeys the $T^{-1/4}$ law whereas the PEPC-$V_2O_5$ ones show visible deviations from this law.

Figure 8 shows voltage-current relationship in the composite and $V_2O_5$ samples, respectively, at room temperature. The characteristics are symmetric, but are non-linear, and their dependence on the voltage, $V$ is given by [19]:

$$I = c \cdot V^B \qquad (2)$$

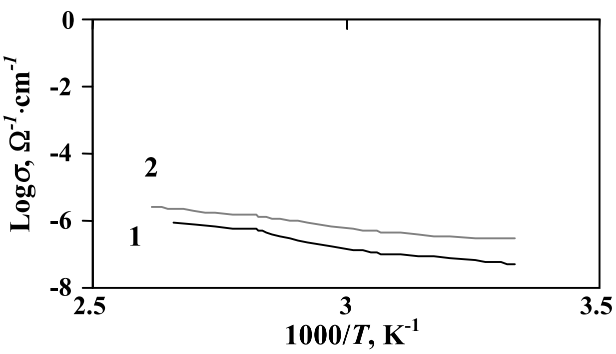


Fig. 5. Conductivity-temperature relationships for the Cu/PEPC-$V_2O_5$/Cu (1) and Cu/$V_2O_5$/Cu (2) samples.

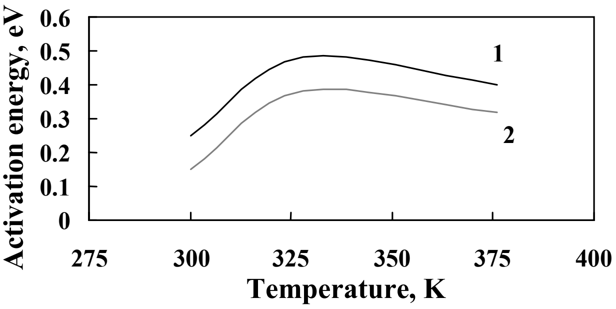


Fig. 6. Dependence of activation energies of Cu/PEPC-$V_2O_5$/Cu (1) and Cu/$V_2O_5$/Cu (2) samples on temperature.

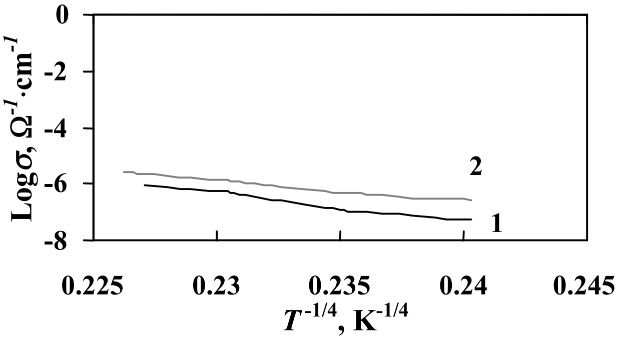


Fig. 7. Plots of log$\sigma$ *vs.* $T^{-1/4}$ for the Cu/PEPC-$V_2O_5$/Cu (1) and Cu/$V_2O_5$/Cu (2) and samples.

where $c$ is a factor of proportionality and $B$ is a nonlinearity coefficient that may be determined from the following equation:

$$B = \frac{(\ln I_2 - \ln I_1)}{(\ln V_2 - \ln V_1)} \qquad (3)$$

where $I_1$ and $I_2$ are the currents measured at voltages $V_1$ and $V_2$, respectively. It was determined that nonlinearity coefficient ($B$) is equal to 1.5 and 2.1 for the composite and $V_2O_5$, respectively.

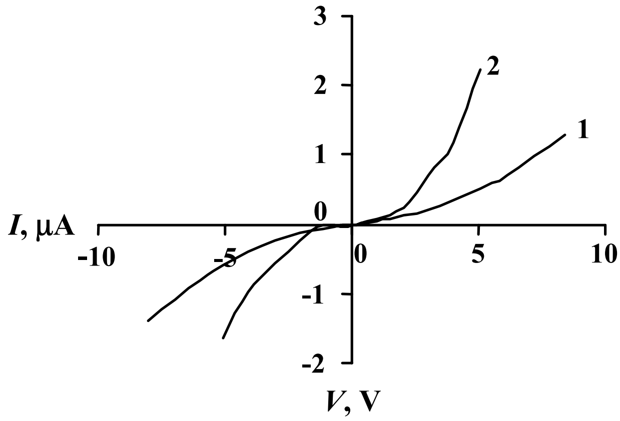


Fig. 8. Voltage-current relationships for the Cu/PEPC-$V_2O_5$/Cu (1) and Cu/$V_2O_5$/Cu (2) samples at room temperature ($T$ = 302 K).

Figure 9 shows voltage-current relationship in the composite at room temperature and $T$ = 100°C: the nonlinearity coefficients in this case were equal to 1.5 and 1.2, respectively, *i.e.* it decreases with temperature.

The nonlinearity of *I-V* characteristics observed experimentally may be caused by several reasons as: (i) increase of conductance of the composite by elect-

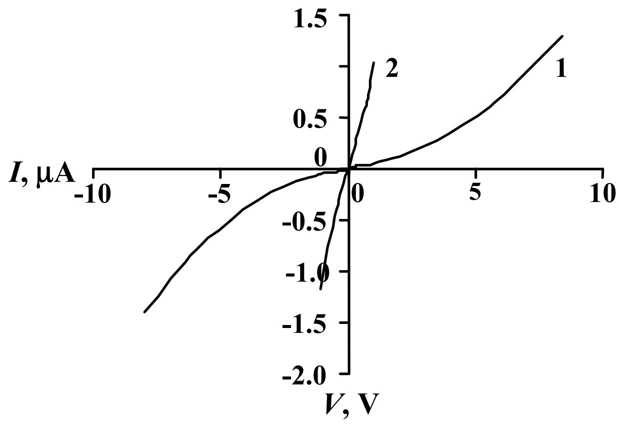


Fig. 9. Voltage-current relationships for the Cu/PEPC-$V_2O_5$/Cu composite at $T$ = 302 K (1) and $T$ = 373 K (2).

ric heating (thermistor's effect), (ii) space-charge-limited currents (SCLC), (iii) effect of electric field [7,8,19] *etc*. The latter case seems has a low probability because of relatively low electric field applied to the samples (it was around of $10^3$ V/cm). In the case of SCLC nonlinearity coefficients are usually greater ($B$ = 2-3) [7,8]. So, the observed nonlinearity behavior of voltage-current characteristics really may be due to the "thermistor's effect" [19], because the $B$ decreases with temperature.

The resistance-temperature relationship in Cu/PEPC-$V_2O_5$/Cu and Cu/$V_2O_5$/Cu samples showed that resistances decrease with temperature, temperature coefficient of resistances of the composite and $V_2O_5$ samples at 27°C are equal to -4.7%/°C and -1%/°C, respectively. As it is large in the case of composite, the composite sample may be used as thermistors.

## Conclusions

In the result of the investigation of Poly-N-epoxypropylcarbazole (PEPC) and vanadium pentoxide ($V_2O_5$) composite, it is found that the DC electrical conductivity, activation energy and non-linearity of voltage-current characteristics of the samples are temperature dependent. It was observed that the temperature dependence of electrical conductivity of the $V_2O_5$ samples on the whole obeys the $T^{-1/4}$ law whereas the PEPC-$V_2O_5$ ones show visible deviations from this law. The PEPC-$V_2O_5$ samples may be used as thermistors as the temperature coefficient of resistance is large and at 27°C is equal to -4.7%/°C.

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