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BEHAVIOR OF UNDOPED POLYANILINE UNDER THE HIGH ELECTRIC FIELD

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Abstract: *The current–voltage characteristics of emeraldine base form of polyaniline (PANI-EB) were studied as a function of film temperature. PANI films were prepared by drop casting method on glazed alumina substrates with interdigital Au electrodes and their DC conductivity was measured. The results indicate that current-voltage characteristics of undoped PANI were nonlinear. The conduction mechanisms in the films in various temperature and voltage ranges were estimated from the behaviour of log I versus $V^{1/2}$ plots. For undoped PANI films, the conduction mechanism appears to be essentially the Schottky type.*
Key words: *polyaniline, DC conductivity, Schottky emission*

1. INTRODUCTION

Although polyaniline (PANI) is a substance known for a hundred years, a great interest in its study came up with the discovery of ability of the electrical current conduction.

The electrical conductivity of polyaniline can be controlled over many orders of magnitude (10^{-10} and 10^{1} $S.m^{-1}$) through acid-base or redox type doping (Fig. 1) (Bhadra et al., 2009).

Due to its excellent environmental stability in the undoped as well as in the doped state, polyaniline in its oxidation state of emeraldine is considered as a very promising material for many industrial applications.

2. CONDUCTIVITY OF PANI-EB

The conductivity of protonated PANI form (emeraldine salt – PANI-ES) has been investigated in details. PANI base form (emeraldine base – PANI-EB) conductivity is studied with lower attention.

Polyaniline emeraldine base is an intrinsic semiconductor with low DC conductivity. Conjugated bonds between carbon and nitrogen atoms allow the charge transport in PANI-EB. In the conjugated bonds, π-electrons create molecular orbitals with the highest electron density in the longitudinal axis of the molecule chain. Due these orbitals, the charge carriers can move along the PANI molecule.

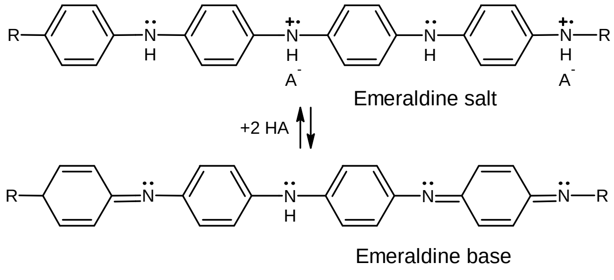

Fig. 1. Conductive (emeraldine salt) and semiconductive (emeraldine base) forms of polyaniline

Cottevieille has first published nonlinear dependence of PANI-EB conductivity in 1995 (Cottevieille et al., 1995).

Pelto studied current-voltage characteristics of EVA/PANI-EB composites and made a comparison with conventional EVA/carbon black composites (Pelto et al., 2004). The new materials show very strong current-voltage nonlinearity. This nonlinear behaviour can be described by the equation (1)

, (1)

where k is the conductivity parameter of the material and α is the nonlinearity coefficient.

Materials with nonlinear characteristics are used for suppressing transients in power supply networks and for electrical stress grading in high voltage applications. Demands for the nonlinearity in terms of α-exponent in these two application areas are different: at least $\alpha = 10$ is required for transients suppressing, materials with lower α are used in stress grading systems (Roberts, 1995).

3. EXPERIMENT

3.1 PANI-EB preparation

Polyaniline was synthesized by chemical polymerization of aniline hydrochloride using ammonium peroxydisulfate as the oxidizing agent. The resulting polyaniline hydrochloride was washed with water and acetone. PANI-ES was deprotonated in aqueous NaOH solution and obtained PANI-EB was dried at 60 °C for 24 hours.

3.2 Sample preparation

PANI-EB films were prepared by dissolving the PANI-EB powder in dimethylsulfoxide to get a 0,1 wt% solution. Thin films were fabricated by drop casting method onto glazed alumina substrates with interdigital gold electrode systems. The solvent was allowed to evaporate at 90 °C under the vacuum for 2 hours. The resulting film thickness after drying was 1 µm. The distance between the opposite electrodes was 30 µm, the thickness of the gold electrode 2 µm.

4. RESULTS AND DISCUSSION

The current-voltage characteristics of the test samples at different temperatures (298, 323 a 353 K) were measured. Measurements were carried out in the range between 0 and 450 V with a Keithley 6517A electrometer, which was also used as a voltage source.

From the results (Fig. 1) it is evident, that the current-voltage characteristics of the PANI-EB are nonlinear and temperature dependent. This nonlinear behaviour can be described by the equation (1). The α coefficient is usually determined from the nonlinear part of the current-voltage curve. In log-log plot, the α expresses the slope of the curve.

In the electrical field with low intensity, the PANI-EB behaves as an insulator. Its conductivity is very low and the current-voltage characteristic is linear according to Ohm's low (the value of α coefficient is approx. 1).

Above the electric field of 3 $kV.mm^{-1}$, the nonlinear behaviour appears, which is caused by the space charge limited currents (SCLC) (Carbone et al., 2005).

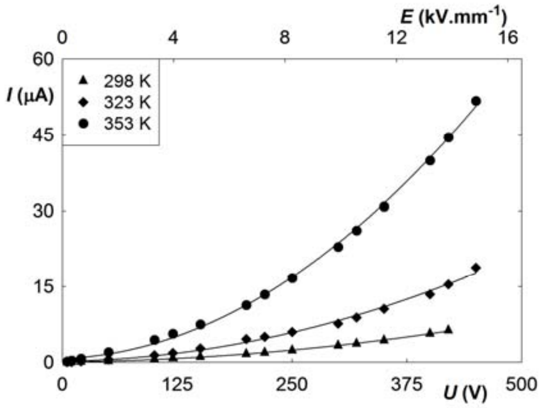

Fig. 2. The current-voltage characteristics of PANI-EB at different temperatures

U	*E*	*α*		
(V)	(kV.mm^{-1})	298 K	323 K	353 K
10	0,33	1,02	0,94	1,03
100	3,33	1,20	1,35	1,15
250	8,33	1,75	1,80	1,90
420	15,0	2,26	2,24	2,82

Tab. 1. The values of the α nonlinearity coefficient at different temperatures and electric field intensities for PANI-EB

In the proximity of the electrode, a space charge is formed due the low mobility of charge carriers. The current density has a quadratic dependence

$$J = \frac{9\varepsilon\mu}{8d^3} E^2, \quad (2)$$

where ε is the polymer permittivity, d the thickness of material and μ the mobility of charge carriers. The quadratic dependence can be seen at 8 kV.mm^{-1} and 353 K (α = 2), which corresponds to the area affected by the SCLC.

In the electric field with intensity of 10 kV.m^{-1}, it is observed that the SCLC model is not sufficient to describe entirely the characteristic (α value at 15 kV.mm^{-1} and 353 K is near 3). The mobility of charge carriers in PANI-EB is influenced by the electric field and the conductivity of polymer can be described by the equation

$$J = J_0 \exp\left(\frac{e\beta\sqrt{E} - \Phi}{kT}\right), \quad (3)$$

where J_0 is the low field polymer conductivity, Φ the barrier height of the electrode-polymer interface, k is the Boltzmann constant, T the thermodynamic temperature and β is an experimentally determined parameter, which characterizes the charge carrier generating mechanism (Kieffel et al, 2000). There are two ways, a Schottky emission (electron injection from electrodes into a polymer) and the Pool-Frenkel mechanism (electron release from electron traps). The beta coefficient values are usually defined as

$$\beta_S = \sqrt{\frac{e}{4\pi\varepsilon_r\varepsilon_0}} \text{ and } \beta_{PF} = 2 \cdot \beta_S, \quad (4)$$

where e is the electron charge, ε is the relative permittivity of the material and ε_0 is the vacuum permittivity (Gould, 2006).

To obtain the information, which phenomena dominates, the values of the β_S and β_{PF} coefficients were determined and the results are compared with the β coefficient calculated as the slope of log I versus $U^{1/2}$ curve (Fig. 3). The theoretical values of the β_S and β_{PF} are β_S = 0,85×10^{-5} eV.m$^{1/2}$.V$^{-1/2}$ and β_{PF} = 1,7×10^{-5} eV.m$^{1/2}$.V$^{-1/2}$. The experimentally obtained values of the β coefficient at temperatures 298, 323 a 353 K are 0,79; 0,9 and 0,94×10^{-5} eV.m$^{1/2}$.V$^{-1/2}$ respectively.

As can be seen, the β_S coefficient coincide better with the experimentally get values of β coefficient. Therefore, it can be said that Schottky emission is the dominant conduction mechanism in PANI-EB, which is in agreement with the results obtained by other authors (Mathai, 2003; Pelto, 2004).

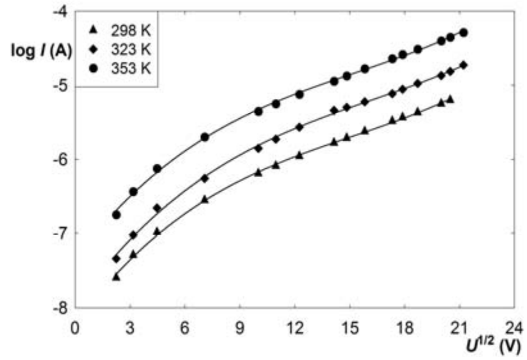

Fig. 3. The current-voltage characteristics of PANI-EB as log I vs. $U^{1/2}$ for the β coefficient determination

5. CONCLUSION

The current-voltage characteristics of PANI-EB at different temperatures were measured. The results show a nonlinear high electric field behaviour of PANI-EB that can be described by space charge limited current model combined with a Schottky emission affected conductivity mechanism. Therefore, PANI-EB appears to be a suitable material for the semiconducting composite coatings used for suppressing transients and for electrical stress grading in high voltage applications. Further research is still needed to see the full potential of PANI-EB in high voltage applications.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

Bhadra, S. et al. (2009). Progress in preparation, processing and applications of polyaniline, *Progress in Polymer Science* Vol. 34, No. 8, 783–810, ISSN 0079-6700

Carbone, A., Kotowska, B. K. & Kotowski, D. (2005). Space-Charge-Limited Current Fluctuations in Organic Semiconductors, *Physical Review Letters*, Vol. 95, No. 23, 236601-236605, ISSN 1079-7114

Cottevieille, D. et al. (1999). Industrial applications of polyaniline, *Synthetic Metals*, Vol. 101, No. 1-3, 703-704, ISSN 0379-6779

Gould, R. D. (2006). Thin Films, In: *Springer handbook of electronic and photonic materials*, Kasap S. O., Capper P. (Ed.), 659-716, Springer, ISBN 0-387-26059-5, New York

Kieffel, Y., Travers, J. P. & Cottevieille, D. (2000). Undoped polyaniline in the high voltage domain: non linear behavior and ageing effects, *Annual Report Conference on Electrical Insulation and Dielectric Phenomena,* Vol. 1, 52-56, ISSN 0084-9162

Mathai, C. J. et al. (2003). Conduction mechanism in plasma polymerized aniline thin films, *Material Letters,* Vol. 57, No. 15, 2253-2257, ISSN 0167-577X

Pelto, et al. (2004). Nonlinear DC voltage-current characteristics of new polymeric composite materials based on semiconductive polyaniline emeraldine base filler, *Proceedings of the 2004 IEEE International Conference on Solid Dielectrics Vol. 2*, pp. 825 - 828, ISBN 0-7803-8348-6, Toulouse, France, June 2004

Roberts, A. (1995). Stress grading for high voltage motor and generator coils, *IEEE Electrical Insulation Magazine*, Vol. 11, No. 4, 26-31, ISSN 0883-7554