Conduction behavior of polyaniline/elastomer composites and the influence of carbon black addition

Björn Sonerud[1], Knut Magne Furuheim[1], Staffan Josefsson[1], Jani Pelto[2], Marjo Ketonen[2], Outi Härkki[2]

[1]Nexans Norway AS, Halden, Norway
[2]VTT Technical Research Institute of Finland, Tampere, Finland

Abstract

Three different compositions of EPDM, polyaniline (PANI) and carbon black have been studied with respect to conduction properties. It could be concluded that both carbon black and polyaniline influence the low field conductivity. In addition, the influence of different conduction mechanisms was studied. Measurements on the temperature dependence of the electrical conductivity indicated that large amount of polyaniline in EPDM rubber manifested in 1D variable range hopping (1D-VRH) behavior whereas less amount, although still well above the percolation threshold, resulted in behavior more similar to the Arrhenius law. However, further studies are necessary to draw definitive conclusions on the influence of filler content. Studying the field dependent conductivity behavior it could be concluded that there is a Ohmic region at low field and a transition towards space charge limited current (SCLC) at higher field with possible influence of other conduction mechanisms.

1. Introduction

Polyaniline is an intrinsically semiconductive polymer which has been studied for use in high voltage applications. Electronic conductivity of PANI is dramatically dependent on the (p-type) doping charge, induced by proton doping. In its non-protonated emeraldine base form has been considered to be one of the more thermally stable conductive polymers which could make it a candidate which could tolerate the demands of high voltage insulation systems. The origin of the semiconductivity (DC $<10^{-9}$ S/cm) observed in highly pure non-protonated PANI is still ambiguous. The main factor influencing the electronic semi-conductivity have been proposed to be the residual (hydrogen bonded) water and solvent molecules acting as proton donors [1]. More recently, quantum chemical calculation has predicted also the influence of PANI crystallinity, chain mobility, and crosslinking. Regardless of the actual mechanism of charge formation, prior impedance measurement suggest that unprotonated PANI supports dipolar relaxation mechanisms based on localized charge carriers (polarons, bipolarons), capable of intra-chain and inter-chain electronic charge transport [2].
The proven semiconductive properties of the materials have indeed proven useful for electrical applications. Applications which have been mentioned are semiconducting layers in cables as well as filler in polypropylene films used in power capacitors [3-6]. Previous publications have also reported a significant nonlinear behavior which is the topic of this paper [5].
Nonlinear behavior mainly has its use in field grading applications, something which is used in, for instance, cable accessories and electrical machines.
When using non-linear PANI-material in composites with electrical insulators it is crucial to have a good understanding of how material processing parameters and different compositions affect the packing and connectivity of the semiconductive materials, and hence the electric properties of the composite. Therefore the influence of different amount of polyaniline in an EPDM matrix as well as the addition of carbon black has been studied with respect to conduction behavior.

2. Method

In this section both measurement techniques and the models used for describing the material behavior is described.

2.1. Sample preparation

The polyaniline used in this study is a high molecular weight grade which has been dried at 85°C for weight stabilization. As matrix material consisting of an EPDM rubber with crosslinking agent was used and for one of the compositions an acetylene carbon black was added. The compounds were prepared in a two roll mill compounder at 70°C for 20 minutes. The polyaniline and crosslinking agent were added to the plasticized EPDM. Samples were checked for voids and good dispersion with SEM imaging.
The compounds were pressed and crosslinked into 60x60x1mm at 190°C for 10 min with preheating (100°C) and 5 MPa pressure. Each test object required roughly 4g of material. The three different compositions discussed in this paper are presented in Table 1.

Table 1: Sample compositions

	PANI (wt%)	Carbon black (wt%)
PANI A	40%	0%
PANI A*	40%	5%
PANI B	50%	0%

2.2 Conductivity measurements

The conductivity of the samples was measured with an HP 4339B electrometer with a 16008B test cell. In order receive sufficient data to map the nonlinear behavior (especially the threshold for onset of nonlinear behavior) four data points for each decade of electric field (10-1000 V/mm) were measured. To ensure stable results logging was performed for three hours at each point amounting a total of 24 h of measurement time per sample.

For the temperature dependent measurement the entire electrometer test cell was placed in an oven. A temperature sensor was placed inside the test cell to make sure that the sample had reached the target temperature before measurements were initiated.

2.3 Temperature dependent models

Both the Arrhenius law and Mott's variable range hopping model has been used to describe the conductivity behavior of polyaniline [7]. The *Arrhenius law* can be expressed as:

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{1}$$

where E_a is the activation energy, T the temperature and k Boltzmann's constant. *Mott's variable range hopping (VRH) model* is described as

$$\sigma(T) = \sigma_0 e^{-(T_0/T)^{1/(n+1)}} \tag{2}$$

with n being the dimensionality of the conduction (1 in the present case), T_0 Mott's characteristic temperature and σ_0 the conductivity at room temperature. Other proposed models such as the activated energy model and the Kivelson model have been omitted from this study [7].

2.4 Field dependent models

Space charge limited current (SCLC) is described as [8, 9]:

$$J = \frac{9}{8}\varepsilon\theta\mu\frac{V^2}{d^3} \tag{3}$$

This is valid for traps at a single discrete energy level. J is the current density, ε the permittivity, d the thickness of the polymer and θ is the ratio of the free carrier density. The function is characterized by being Ohmic conduction at low field exhibiting k=1 in an electric field (E) vs. current density (J) plot. When space charge limited conduction dominates k=2 [10].

3. Results

3.1 Low field conductivity

Looking at the low field conductivity of the compositions studied here it can be seen that the addition of carbon black or higher amount of polyaniline will increase the low field conductivity (Table 2). This can be related to another study [11] where a clear log-linear relationship between conductivity and amount of carbon black was observed whereas the influence of increasing amount of polyaniline is more ambiguous.

3.2 Temperature dependent models

In Figure 1 the Arrhenius behavior of the three different compositions at low field (100V/mm) is shown and in Table 3 the activation energy (E_a) and coefficient of determination (R^2) for the fit is shown (1.0 being a perfect fit). If the same behavior is plotted for field strength of 1 kV/mm instead the results are as shown in Figure 2 and Table 4. It is difficult to visually observe any difference between the different field strengths and models (i.e. Arrhenius and 1D-VRH) , hence the results of the fitting for variable range hopping is shown only in Table 5 and 6.

3.3 Field dependent models

In Figure 3 and 4 the normalized current density (J) is plotted vs electric field (E) and the low and medium field behavior is fitted with a linear function. The transition threshold between the different field regions is determined visually and should therefore be considered as an approximation (as indicated in Table 7 and 8 where the results from the fitting are presented).

Table 2: Low field conductivity at room temperature (100 V/mm).

	σ^1
PANI A	1
PANI A*	10
PANI B	17

[1] Normalized with respect to conductivity of PANI A.

Table 3: Arrhenius behavior at low field (100 V/mm).

	E_a	R^2
PANI A	0.58	0.9998
PANI A*	0.35	0.9422
PANI B	0.31	0.9977

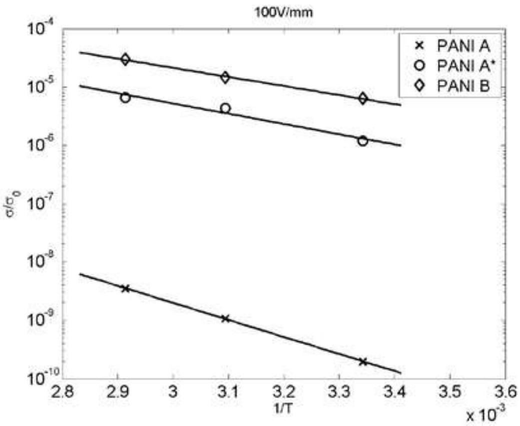

Figure 1: Arrhenius plot of the conductivity behavior at low field (100 V/mm).

Table 4: Arrhenius behavior at medium field (1kV/mm).

	E_a	R^2
PANI A	0.48	0.9999
PANI A*	0.30	0.9653
PANI B	0.25	0.9919

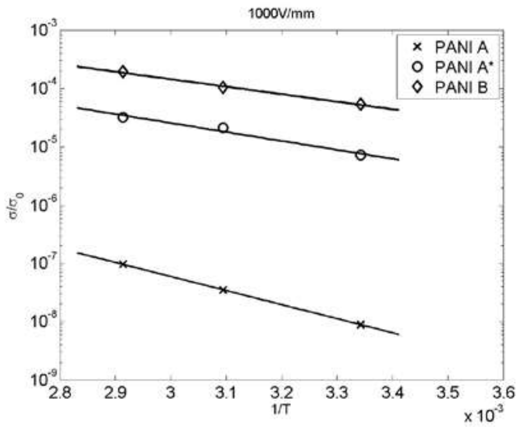

Figure 2: Arrhenius plot of the conductivity behavior at medium field (1 kV/mm).

Table 5: 1D-VRH at low field (100 V/mm).

	T_0	R^2
PANI A	$5.59 \cdot 10^5$	0.9994
PANI A*	$1.61 \cdot 10^5$	0.9367
PANI B	$2.04 \cdot 10^5$	0.9987

Table 6: 1D-VRH at medium field (1kV/mm).

	T_0	R^2
PANI A	$3.85 \cdot 10^5$	1.0000
PANI A*	$1.55 \cdot 10^5$	0.9611
PANI B	$1.09 \cdot 10^5$	0.9939

Table 7: Linear fit of conduction behavior at low field and room temperature.

	k	E_T (approximate)
PANI A	1.0	50 V/mm
PANI A*	1.2	20 V/mm
PANI B	1.1	20 V/mm

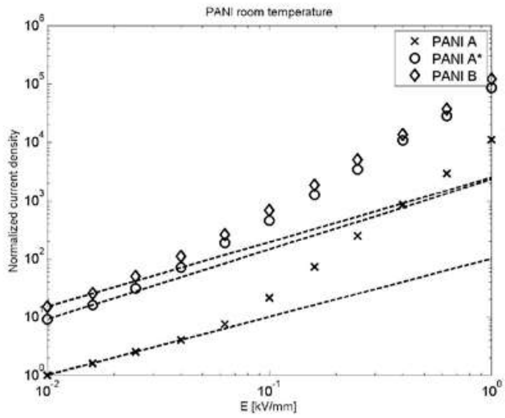

Figure 3: Field and normalized current density plot with linear curve fit of low field relationship.

Table 8: Linear fit of conduction behavior at medium field and room temperature.

	k	E_T (approximate)
PANI A	2.7	50 V/mm
PANI A*	2.2	20 V/mm
PANI B	2.1	20 V/mm

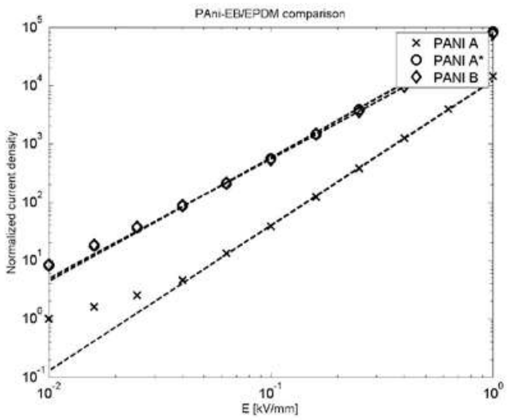

Figure 4: Field and normalized current density plot with linear curve fit of medium field relationship.

4. Discussion

Taking another study into consideration [11], there is a strong indication of the relationship between the amount of carbon black and the low field conductivity of the compound. There are also strong indications of synergy effects between carbon black and polyaniline [11].

Looking at the general results from the fitting of the temperature dependent models the Arrhenius behavior seem to be a marginally better description of the PANI A and PANI A* than the 1D-VRH. The PANI B compound shows a slightly better fit for the 1D-VRH. This is in accordance with literature [8] where PANI-EB in its pure form has been shown to follow a 1D-VRH behavior. It can therefore be expected that an increase of polyaniline content in a composite will make the behavior more similar to that of the pure form. However, it should be noted that the amount of temperature data is limited (three points in this study) and consequently the fitting will be sensitive to any noise or disturbance during the measurement.

Considering the electric field vs. current density plots the low field behavior is Ohmic (k=1.0- 1.2) whereas the medium field behavior is in the high range of what could be expected of space charge limited current (k=2.1-2.7) which could indicate the influence of some other conduction mechanism than pure SCLC. Also, there is some indication that a higher amount of conducting particles, both polyaniline and carbon black, will influence the threshold value of the transition to the nonlinear regime but this needs to be verified in further studies.

5. Conclusions

Carbon black and polyaniline can be used to influence the low field conductivity levels of EPDM compounds. The results suggest that the increase of conductive particles in the matrix could affect the threshold value for transition from Ohmic conduction to SCLC but this needs further investigation. A higher amount of polyaniline tends to shift the thermal behavior more towards a 1D-VRH rather than Arrhenius behavior and there are indications that there can be other conduction mechanisms than pure SCLC acting under increasing field strength.

6. References

[1] Matveeva, E.S. “Residual water as a factor influencing the electrical properties of polyaniline: The role of hydrogen bonding of the polymer with solvent molecules in the formation of a conductive polymeric network” *Synthetic Metals,* vol. 79, n.2, 77-81, 1996. 127-39.

[2] Pinto, N.J., Acosta, A.A., Sinha, G.P., Aliev, F. M. ”Dielectric permittivity study on weakly doped conducting polymers based on polyaniline and its derivatives” *Synthetic Metals,* vol. 113, n.2, 77-81, 2000.

[3] Cotteville, D., Le Méhaute, A., Challioui, C., Mirebeau, P. and Dernay, J.N., “Industrial applications of polyaniline”, *Synthetic Metals*, v. 101, pp. 703-704, 1999.

[4] Cottevieille, D., Cariou, F, Mirebeau, P., Demay, J.N. and Parasie, Y., “New potentialities of conductive polymers for cables”, *Proceedings of 8th International Conference on Power Insulated Cables (Jicable 99)*, Paris, France, pp. 845-848, 1999.

[5] Kannus, K., Harju, P., Lathi, K., Pelto, J. and Paajanen, M., ”Electrical Properties of Polypropylene and Polyaniline Compounds”, *Proceedings of the 2004 International Conference on Solid Dielectrics (ICSD 2004)*, Toulouse, France, pp. 67-70 , 2004.

[6] Kieffel, Y., Travers, J.P., and Cotteville, D., “Undoped polyaniline in the high voltage domain: Non linear behavior and aging effects”, *Proceedings of the 2000 Conference on Electrical Insulation and Dielectric Phenomena (CEIDP 2000)*, Victoria, Canada, pp. 52-56, 2000.

[7] Mzenda, V. M., Goodman, S. A. and Auret, F. D., “Conduction models in polyaniline – The effect of temperature on the current-voltage properties of polyaniline over the temperature range 30 <T(K) >300”, *Synthetic Metals*, vol. 127, 285-289, 2002.

[8] Nazeer, K, Jacob, S., Thamilselvan, M., Mangalaraj, D., Narayandass, S. and Yi, J., “Space-charge limited conduction in polyaniline films”, *Polymer International*, vol 53, 898-902, 2004.

[9] Sessler, G. M., Hahn, B., and Yoon, D. Y., “Electrical conduction in polyimide films”, *Journal of Applied Physics*, vol. 60, n. 1, 1996.

[10] Auckland, D. W., Su, W. and Varlow, B. R., “Nonlinear fillers in electrical insulation”, *IEE Proc. Sci. Meas. Technol.*, vol. 144, n. 3, 127-133, 1997.

[11] Sonerud, B., Josefsson, S., Furuheim, K-M, Boyer, L., Frohne, C., Pelto, J., Härkki, O., Ketonen, M., “Nonlinear electrical properties and mechanical strength of EPDM with polyaniline and carbon black filler”, unpublished, to be presented at the *2013 International Conference of Solid Dielectrics (ICSD 2013)*, Bologna, Italy.