STUDY OF ANISOTROPY AND INHOMOGENEITY OF ELECTRICAL PROPERTIES OF CARBON BLACK – POLYSTYRENE COMPOSITE LAYERS

Jan LIPTÁK, Josef SEDLÁČEK, Ivana PILARČÍKOVÁ, Václav BOUDA
CZECH TECHNICAL UNIVERSITY IN PRAGUE, Technická 2, 166 27 Praha 6,
Liptak@fel.cvut.cz, Sedlacek@fel.cvut.cz, Pilarcik@fel.cvut.cz, Bouda@fel.cvut.cz

Abstract

If carbon black (CB) concentration increases in polymeric matrix, the composite sharply changes its electrical properties (conductivity, permittivity). When the CB content reaches the percolation value, the composite is transformed from insulating into conducting state due to continuous CB network formation in polymer matrix. CB agglomeration is strongly influenced by particles distribution. This work deals with homogeneity and anisotropy of electrical properties both in normal and planar direction respectively in CB – PS (polystyrene) composites. Electric field was used for stimulation of anisotropy of CB agglomerations. CB for our samples was cleared of absorbed water and partially of residual ions. Plate composite samples were prepared from solution of PS in toluene. After toluene evaporation up to constant weight aluminium contacts were deposited onto both upper and bottom sample surface respectively. Sheet resistance, respectively volume resistivity was measured by Van der Pauw, respectively ASTM D257-66 method at room temperature. Impedance analysis was carried out in the frequency region from $10^{-1}$ Hz to $10^{8}$ Hz. Impedance analysis in planar direction was carried out in temperature region from 0 °C to 100 °C. The results of dielectric measurements were interpreted in terms of complex permittivity components when the sample was substituted by parallel circuit of resistance and capacitance. For sheet measurements the new quantities (proportional to complex permittivity) were defined and used.

Keywords: carbon black, polymer composites, impedance analysis

1. INTRODUCTION

If electrical conductive filler (carbon black (CB)) is used for polymer composite material preparation, the resulting sample electrical properties can change from insulator to conductor. When the percolation concentration of CB is reached, the continuous bulk network structure is formed in the composite. Conductivity dependence on CB concentration shows the sharp rise [1] (percolation threshold). Conductivity can change in the magnitude of several orders due to continuous CB network formation in the composite. The composites of conductive polymers with fullerenes are intensively studied for solar cells applications [2]. Also, the network in the bulk increases the viscosity [3] of the composite. CB network formation is affected by many parameters as kind of polymer [2], properties of carbon black [4] (density, surface area, composition), ion concentration [5, 6], pH value, external electrical field [5, 7, 8], gravitational field (when the sedimentation takes place). The composites with CB with lower concentration of ions show higher electrical conductivity and more fine structure than composites with usual CB [6]. In electric field carbon black particles tend to form the chains according the force lines of external field [5, 8]. In the layer samples of CB – polymer composites prepared from solution the CB network structure depends also on time of evaporation of the solvent CB [5]. CB agglomerates are seemed to be smaller and form more fine structure. Their electrical conductivity is higher in comparison with the samples evaporated quickly. Both magnitude and mechanism of conductivity depend on CB concentration. Electrical conductivity of the samples with lower CB content is smaller and shows non-ohmic behaviour in comparison with the samples with higher CB concentration [6]. Non-ohmic behaviour was detected by V-A curves and by the frequency dependences of imaginary part of complex permittivity in logarithmic scale. Both curves are linear for the samples with higher CB loading. It was suggested that CB agglomerates are separated by thin polymer layer. Therefore, the mechanism of conductivity is not ohmic but probable quantum tunnelling or breakdown takes place.
The measurement of electrical or dielectric properties is very sensitive method for detection of conductive network or CB agglomerates formation. On the other hand, the actual measured values are strongly affected by many external (contact between electrode and CB, arrangement of measurement condenser, frequency, voltage etc.) and internal (connection of CB particles) conditions. CB agglomerates are created due to Van der Waals forces randomly (without external field) in the bulk with unlike diameters and mutual contacts. Therefore, in principle, the material is not homogeneous and isotropic (if an external field is applied during the sample preparation). This work deals with inhomogeneity and anisotropy of CB – PS (polystyrene) composite layers.

2. SAMPLE PREPARATION

Five samples with CB concentrations 1, 3, 5, 6 and 7% were prepared from the solutions of 3 g of PS (granulated solid) in toluene and corresponding amount of CB. Before mixing, CB was dried on the hot plate HP 01 at 120 °C up to constant weight. For pulverisation and homogenisation the rotational homogenizer IKA (speed 20000 rpm for 2 min.) and ultrasonic homogenizer Sonopuls UW 3200 (Bandelin with the power 40 W for the time 2 x 1 minutes) were used. During pulverization and homogenization the composite had to be cooled because the temperature of the non-cooling sample rose up to 50°C after mechanical pulverisation and up to 70°C after ultrasonic homogenisation. Then the liquid composite PS – CB – toluene was coated directly into the Petri dishes with diameter 70 mm. After toluene evaporation up to constant weight the plate samples with the diameter 40 mm and the thickness from 0.05 to 0.3 mm were broken up.

3. ELECTRICAL MEASUREMENT

For electrical measurements the contacts were prepared by the method of vacuum evaporation deposition of aluminum in the form for Van der Pauw method measurement (Fig. 1b) and after that for three electrode system (ASTM) measurement (Fig. 1a). The electrode arrangement according Fig. 1a allows the measurements both in normal and planar direction respectively. Bulk resistivity $\rho$ (ohm.m) was evaluated using the formula (Eq. 1):

$$\rho = \frac{U}{I} \cdot \frac{\pi \cdot D_1^2}{4t} \quad \text{Eq. 1}$$

where $U$ (V), $I$ (A), $D_1$ (m), $t$ (m) are measuring voltage, current, guarded electrode diameter, sample thickness and where electric field was applied between guarded (G) and unguard (U) electrodes. Guard electrode (g) increases homogeneity of electric field. If external field is connected onto the electrodes (G) and (g), the surface resistance $R_{sur}$ can be evaluated according the formula (Eq. 2):

$$R_{sur} = \rho_{sur} \frac{D_2 - D_1}{\pi(D_1 + D_2)} \quad \text{Eq. 2}$$

Resistivity obtained from sheet resistance was measured by Van der Pauw method (Fig. 1b). $R_{ABCD}$ is defined as the portion $U_{CD}/I_{AB}$, where $I_{AB}$ is the current flowing between contacts A and B and $U_{CD}$ is the potential difference measured between C and D points. We used four possible connections and commutated
the electric current and we obtained 8 values for evaluating the resistivity \( (Eq. \ 3) \). The sheet resistivity was calculated according the formula:

\[
\rho_{\text{sheet}} = \frac{1}{8} \cdot \frac{\pi \cdot t}{\ln 2} \cdot (R_{ABCD} + R_{BADC} + R_{BCDA} + R_{CABD} + R_{DCBA} + R_{DCBA} + R_{DABC} + R_{ADCB}) \quad Eq.\ 3
\]

In alternate electric field the measured values of impedance \( Z \) and phase \( \phi \) were transformed to parallel capacity \( C \) and resistance \( R \) and expressed by the terms of complex permittivity \( \varepsilon^* = \varepsilon' - i \varepsilon'' \), where real part \( \varepsilon' \) represents relative permittivity \( \varepsilon_r \) and imaginary part \( \varepsilon'' \) represents dielectric losses.

\[
\varepsilon' = \frac{4t}{\pi \cdot \varepsilon_0 \cdot D_1^2} = \frac{\sin \phi}{Z \cdot \omega} \cdot \frac{4t}{\pi \cdot \varepsilon_0 \cdot D_1^2} \quad Eq.\ 4
\]

\[
\varepsilon'' = \frac{4t}{\varepsilon_0 \cdot \omega \cdot \pi \cdot D_1^2} \left[ \frac{\cos \phi}{Z} + \frac{1}{R_{dc}} \right] \quad Eq.\ 5
\]

If \( R_{dc} \) is dominant, the plot of \( \varepsilon'' \) versus \( \log f \) is linear with the slope -1. All measurements were carried out by the RCL meter Fluke PM 6306, LCR HiTester Hioki 3522-50 and LCR meter Agilent 4284A.

4. RESULTS AND DISCUSSION

Pulverised and dispersed CB particles in a solution intensively tend to agglomerate to form the larger particles due to Van der Waals forces. Intensity of this attraction is proportional to the interaction area. Therefore homogeneity and structure of composites depend on quality of CB pulverisation and dispersion.

On the sample surface the planar structure was observed on AFM electrical potential pictures \( \text{Fig. 1, Fig. 2} \). The CB agglomerates are projected to electrical potential peaks. We can compare the samples with different CB concentrations. The concentration, distribution and heights of the peaks reflect the concentration, distribution and diameter of CB agglomerates. It is clear that the inhomogeneity is more visible on the samples with lower concentration of CB.

**Fig. 2** AFM electrical potential (horizontal dimensions and scale values are given in brackets) for the samples (from left) with 0 % CB (10x10 \( \mu \)m, 0,843 V, 2,951 V), 1 % CB (10x10 \( \mu \)m, -0,949 V, -0,053 V, 0,844 V) and 3 % CB (20x20 \( \mu \)m, -1,269 V, -0,387 V, 2,043 V).

**Fig. 3** AFM electrical potential (horizontal dimensions and scale values are given in brackets) for the samples (from left) with 5 % CB (10x10 \( \mu \)m, 0,791 V, 2,007 V, 3,223 V), 6 % CB (20x20 \( \mu \)m, -1,45 V, 0,105 V, 1,661 V) and 7 % CB (20x20 \( \mu \)m, 1,299 V, 4,083 V, 6,867 V).
The samples prepared from solutions can be expected to be inhomogeneous in normal direction due to CB sedimentation during solvent evaporation. This expected behaviour was not observed. The optical microscope observations in dark field of the fracture surface show practically reciprocal results (Fig. 4). Somewhat higher concentration of CB is seemed to be in upper surface of the sample. Also there are differences between the structures of CB in polymer in upper and bottom surface layers. Upper surface image shows more agglomerated structure than bottom one. On the other hand, the bottom surface structure is more fine agglomeration. We believe that it corresponds with higher time of the solvent evaporation due to more diluted solution of PS was used. This observation is in a good agreement with our previous results [5], where the composite solutions in covered Petri dishes required longer time of solvent evaporation.

Fig. 4 Optical microscope pictures of the fracture composite upper (left) and bottom (right) surfaces of the sample with 6% CB. Dark field. Magnification 600.

Electrical properties of the samples in planar direction are reasonably affected by the structure and anisotropy of CB in polymer matrix. When electric field is applied, CB tends to form the chains. But the electrical conductivity is very small for the CB concentration 1% due to separation of the chains by polymer (Fig. 5). The reasonable increase of conductivity (decrease of resistivity) was detected for the samples with 3% CB (Fig. 6). Resistivity of both samples with 1% CB and 3% CB is lower for those ones prepared (evaporated) in electric field 280 V/cm. Note that percolation theory gives the percolation concentration of CB about 16%. Chains formation of CB in electric field reasonably decreases the percolation concentration. Resistivity difference due to application electric field is about one order in magnitude for the samples with 1% CB and about two orders in magnitude for the samples with 3% CB. Also Fig. 6 shows that the resistivity decreases with measuring voltage. The slope of the decrease expressed by the fraction of resistivity measured at 0.5 V and 2 V increases from the value 1.06 for 1% CB to 2.6 for 7% CB (Fig. 7). These results reflect non-ohmic charge transport in the composite. We suggest electron hopping or quantum mechanics tunnelling mechanism of charge transport between CB agglomerates through the thin insulating layer between them.

Fig. 6 Resistivity (ohm.m) of the samples with 1% and 3% CB prepared without el. field and in electric field 280 V/cm as a function of measuring voltage. Thickness of the samples was 0.3 mm.

Fig. 7 Conductivity (S/m) of the sample with 7% CB as a function of measuring voltage. Thickness of the samples was 0.3 mm.
The impedance – phase response is more complicated because space charge polarisation in CB agglomerates takes place too. It is reflected in the frequency dependences of complex permittivity components (Fig. 8, Fig. 9). Real part (relative permittivity) monotonically decreases with increasing frequency. Imaginary part $\varepsilon''(\text{eps}'')(\text{in logarithmic scale})$ shows the linear behaviour with the slope -1 for the frequencies lower than 1 kHz for the samples with 1% CB. The samples with higher content of CB behave linearly for the frequencies lower than 10 kHz. We believe that this frequency corresponds with CB agglomerates diameters and mutual connections between them.

![Fig. 8 Dependences of relative permittivity of the composites on frequency with denoted CB loading](image1)

![Fig. 9 Dependences of imaginary part of complex permittivity of the composites on frequency with denoted CB loading](image2)

5. CONCLUSION

The samples of CB – PS composites prepared by evaporation of toluene in the form of thin plates show the similar electrical properties as bulk ones. Electrical conductivity, relative permittivity and dielectric losses sharply rise with increasing CB content. The measuring voltage dependence of conductivity and impedance shows to non-ohmic mechanism of charge transport inside and between CB agglomerates. Also, the frequency dependences of the complex permittivity components show to space charge polarization. There are differences between the bulk resistivity, surface resistivity and sheet resistivity in magnitude, but their dependences on CB concentration and measuring voltage are qualitative same. Therefore the charge transport mechanism is the same in both normal and planar direction respectively.

Homogeneity of the samples is given by pulverization and distribution of CB particles in polymer and by level of their agglomeration. These phenomena were observed on optical microscope and AFM pictures. It was shown that quick toluene evaporation results to quick agglomeration of CB. Application of electric field during toluene evaporation results to chain structure of CB agglomerates and increases electric conductivity.

LITERATURE