DIELECTRIC PROPERTIES OF CARBON BLACK – POLYSTYRENE COMPOSITE THIN LAYERS

DIELEKTRICKÉ VLASTNOSTI KOMPOZITNÍCH TENKÝCH VRSTEV NA BÁZI SAZE - POLYSTYREN

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Abstract

The dielectric properties of composite materials of polystyrene (PS) – carbon black (CB) prepared from solution in toluene by coating procedure were studied in the frequency region 100 Hz to 1 MHz and temperature interval 25 to 100 °C.

Ve frekvenčním oboru 100 Hz až 1 MHz a teplotním intervalu 25 – 100 °C byly měřeny dielektrické vlastnosti kompozitních tenkých vrstev na bázi saze – polystyrene připravených z roztoku naléváním.

Key words

polymer composites, carbon black, dielectrics, frequency spectra, temperature spectra, complex permittivity,

polymerní kompozity, saze, dielektrika, frekvenční spektra, teplotní spektra, komplexní permitivita

Introduction

The composite materials on the base of polymer-inorganic compound are widely used in industry. They combine the properties of polymer matrix and filler. In addition, the mutual interactions between two or more compounds are important for the resulting composite features. When the filler is electrically conductive, a micro-electronic and nano-applications are reasonable. Many publications were dealt with the metal – polymer composites, but very interesting and prospective material is carbon. Both regular structure of fullerenes or nano-tubes and very complicated arrangement in carbon black (CB) provide wide structural varieties. Properties of carbon black (CB) – polymer systems have been studied for several decades[1-6]. It was reviewed a number of works dealing with the increasing values of viscosity[1, 2] and electrical conductivity[3-] of the composites when the CB contents increase.

When the concentration of the filler in the composite reaches the percolation value the conductive network is formed. Dependences of conductivity on CB concentration show the sharp rise[1] (percolation threshold). Also, the network in the bulk changes the mechanical properties (viscosity increases[2]). The value of the percolation concentration depends on the materials used (type of polymer[3, 11], kind of CB - specific surface area[6], electric charge, particle size and their distribution, etc.) and sample preparation technique (the speed and time of dispersion (shearing), temperature, concentration of added salt, ultrasound acting[14], intensity of applied electric field[15]). Therefore the published percolation concentration values are in broad interval 0,03 – 20 vol.%. The increase of conductivity is presented from a few to 12 orders of magnitude. The kinetics of the conductive CB network formation can be observed in time-conductivity dependences at constant CB content. When the temperature of the composite is higher than melting point, the percolation network formation can be detected by sharp increase of conductivity in the "percolation time" [12, 13]. The composite of CB – polymer is poly-disperse system of CB particles. The primary CB particles are about 30-50 nm in diameter, but part of them is agglomerated into agglomerates with diameter 100 nm and more. They can move through the polymer matrix due to thermal motion and connect mutually. The motion possibility is influenced by viscosity of polymer and it is controlled by temperature. With decreasing viscosity of the melt the percolation CB content shifts to the lower values[11]. When temperature is cycled, hysteresis of resistivity can be observed[4]. Also, polymers with lower values of surface tension surround the CB more intensive and hinder their agglomeration. Therefore the melts with higher surface tension show higher values of the percolation concentration[11]. Due to applied electric field large dipoles are induced and therefore the polar aggregates can mutually connect into a chain structures between electrodes. The growth of dendrites from the anode was observed. The increase of voltage applied to composite at liquid state results to lowering the percolation time[15].

Properties of carbon black from different producers are unlike quality. CB is characterized by the size of particles, specific surface area, and electrical conductivity and so on. For CB with higher surface area the lower percolation concentration was observed[6].

The theoretical explanation of the phenomenon mentioned above was based on statistical percolation theory. Only statistically distributed spherical shaped particles without any interactions were taken into account. In result, the percolation concentration 16 vol.% CB was obtained. But it is not true for CB particles. During manufacturing, the CB particles obtain electric charge, usually negative. More rigorous theory is based on colloidal coagulation. It supposes non-spherical particles, attractive Van der Waals and repulsive Coulomb forces between them. The application of the colloidal theory onto CB coagulation was described in 1996[12]. Both Coulomb and Van der Waals forces in equilibrium result to potential barrier between particles. The contact of the particles can take place by two ways. Firstly, shear forces produced by stirring can surmount the energy barrier or adding salt[12] can reduce the barrier. The ions added into composite deform the ionic atmosphere and CB contact is possible. When the ions are added in salt[12] or they penetrate from electrodes to the sample, the similar results are obtained[, 13].

From the electrical point of view, the impedance response is very complicated. The conductivity of graphite hexagonal layers is given by p-electrons and is quite high, but in CB particle they are broken and situated in unlike directions. We can suppose that the similar structure is in a crystal with very high concentration of defects. But the main role for the conductivity of the composite is played by quality of the CB particle contacts in polymer matrix. At lower concentration of CB the aggregates are insulated by polymer and they are able to polarize. Hence, it causes the capacitive behaviour of the composite. At the percolation threshold the material is changed from insulator to conductor. Therefore the impedance analysis of these systems should reflect both the contacts quality between CB particles and the size of the CB clusters (network). This behaviour can be described by complex conductivity as well as complex permittivity. The frequency dependencies of the components of complex permittivity show the characteristic behaviour of the space charge polarization. High values of ε' are observed at low frequencies and ε'' is strongly influenced by *dc* conductivity[9].

Experimental

All results mentioned in the introduction part of the paper were obtained on the samples prepared from the melt. Polymer was mixed with CB above the polymer melting point. Hence the shear forces during stirring process were the main factor for distribution of the CB particles. For following coagulation process, viscosity (~ temperature) is controlling parameter. On the other hand, thermal motion of polymer segments causes the breaks of the conductive network in the composite (PTC effect). We believe that similar conditions for migration of CB agglomerates are in polymer solution. Viscosity of the composite is controlled by the polymer concentration and the shear forces are also applied by stirring the sample in liquid state. Soaking the CB particles with the solvent makes their distribution easy due to surface tension forces cause the micro-breaks in the CB.

Sample preparation:

Preparation of the samples in this work was curried out in four steps. Firstly, CB was soaked in the toluene solvent for a few days. Secondly, the CB was mixed with the solution of 5 g of polystyrene in toluene. The beaker was filled with toluene up to the volume of 80 cm^3 to be able homogenizer head dipping enough. CB was dispersed and pulverized by IKA rotational homogenizer at speed 20000 rpm for the 3 minutes. After that, the ultrasonic homogenizer Sonopuls UW 3200 (Bandelin) was used with the power 40 W for the time 3 x 5 minutes. The series of liquid precursors with CB concentration from 0,5 to 4 w% were prepared.

For preparation of our samples the carbon black CHEZACARB EC produced by Chemopetrol Group j. s. c. (Czech Republic) and polystyrene BRALEN produced by Kaučuk j. s. c. (Czech Republic) were used. The amounts of all substances (CB, PS, toluene and mixtures) were controlled by weight with accuracy of 0,01 g or 0,0001 g. The concentration is given by mass fraction *w* or weight percent.

Electrical measurements:

The composite layers were prepared on the printed circuit cards after toluene evaporation up to the constant weight. The copper printing on the card was in the form of two mutually dipped racks. The width of the layer between copper electrodes was d=1 mm and its total length on the card was l=1800 mm. For comparison the other card with d=2 mm and the same length was used. The thickness of the layer was 30-40 μm. The sample was put on the hot plate HP 01 and the temperature was controlled in the interval 25 – 100 °C.

For the measurements in the parallel plate condenser the plate samples of the thickness 30 – 100 μm and diameter 40 mm were prepared after toluene evaporation in the Petri dishes.

The impedance analysis in the frequency region 50 Hz to 1 MHz was carried out with the PM 6306 RLC meter FLUKE at 1 V (all samples were tested at the voltage interval 0,1 – 2 V). Without any reasonable results the measurement frequencies up to 10MHz and down to 10 mHz were applied with HIOKI 3535 LCR HiTESTER and HIOKI 3522-50 LCR HiTESTER. In the view of measurement precision these results are not presented. Also, the *dc* conductivity of all samples was tested with HIOKI Hi tester. All displayed values of *dc* conductivity were out of range of the tester.

From impedance-phase Z-φ measurements the conductance $G(S)$ and capacity $C(F)$ were calculated in the parallel scheme according equations:

$$C = \frac{-\sin\varphi}{Z\omega} \quad , \quad G = \frac{\cos\varphi}{Z\omega}, \qquad \text{Eq. 1}$$

where $\omega = 2\pi f$ is angular frequency.

Results of the measurements are presented in the terms of complex permittivity:

$$\varepsilon^* = \varepsilon' - j\varepsilon'', \qquad \text{Eq. 2}$$

where real component ε' is called relative permittivity ε_r or dielectric constant. It can be expressed by the rate of the capacity of the condenser filed with dielectric and condenser filled with vacuum (air). By this way the ε_r was evaluated from the measurements of the plate samples in the plate condenser. The imaginary part ε'' represents the loss current component, which is in phase with applied voltage. It can be written as:

$$\varepsilon'' = \frac{\sigma + \sigma_{dc}}{\omega\varepsilon_0}, \qquad \text{Eq. 3}$$

where σ is *ac* conductivity (dielectric Maxwell displacement) and σ_{dc} is *dc* component of the conductivity. From the theory of dielectrics it is well known that in the case of rotational dipole polarization ε' fall down and ε'' shows the maximum when the frequency of external electric field equals to “relaxation frequency” of the material.

The dielectric response of many materials differs from that. There are many cases where the both real and imaginary parts of complex permittivity follow the power low in the form:

$$\varepsilon' = A \cdot f^B, \ \varepsilon'' = A \cdot f^B, \qquad \text{Eq. 4}$$

where A and B are constants.

With regard for the sample dimensions on the cards and definition of complex permittivity we defined the following quantities:

$$e1 = \frac{Cd}{\varepsilon_0 l}, \quad e2 = \frac{Gd}{\varepsilon_0 l\omega}, \quad tg = \frac{e2}{e1}, \qquad \text{Eq. 5}$$

where *e*1 (*e*2) is similar as real (imaginary) component of complex permittivity, and *tg* can be interpreted as loss factor.

Results and discussion

The results of this work can be presented in the following paragraphs.

The resulting values of capacity, conductance (Eq. 1) and *e*1, *e*2 (Eq. 5) were not influenced by measuring voltage in the interval 0,1 – 2 V. The deviations of all quantities with voltage changes were less than 1%.

The results of the samples with 0,5 w% of CB showed too small values of *C* and *G*. It was not possible to eliminate the impedance of the clean card correctly. On the other hand, the samples with 3w% of CB and more showed conductive behaviour without capacitive part. Therefore in this work the data for the samples with 1w% and 2w% of CB are presented only.

The thicknesses of the plate samples were evaluated as average value from ten measurements at different places. The thickness increase with increasing mass of the polystyrene with 1 w% CB per unit area is illustrated in Fig.1. The average bulk density computed from these data is 955 kg/m^3 +-7%. Similar curves and the values of density were observed for the samples with 2w% of CB. The deviations are in experimental errors.

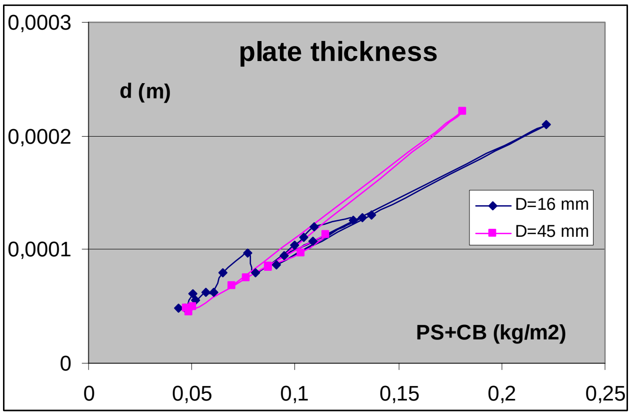

Fig.1. *The thickness of the plate samples (1w% CB) with denoted diameter D as a function of the PS+CB mass per m*^{2}

The relative permittivity of plate samples obtained from direct capacity measurements is not independent on the sample thickness. It is typical result for this kind material – composites with conductive component. Relative permittivity increases with increasing thickness (Fig.2). The samples with 2w% of CB show higher permittivity than the samples with 1 w% of CB and the slope of the curve for 2 w% is much higher.

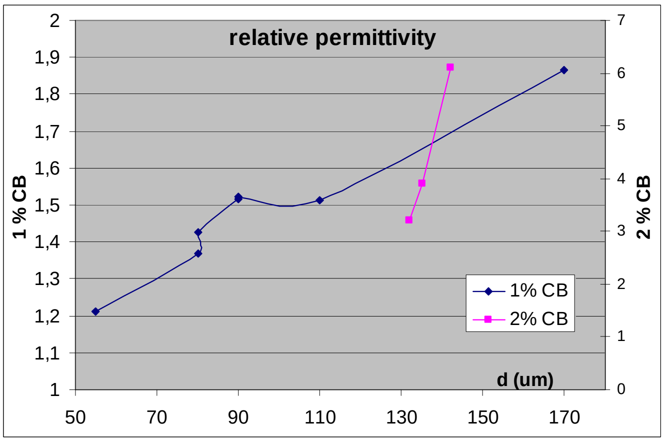

Fig.2. *Dependences of relative permittivity as a function of sample thickness with denoted CB content. Frequency 1 kHz.*

The different results were obtained on the samples on cards. The frequency dependencies of *e*1 of the samples with 1 w% CB were monotonically decreases. For the samples with 2 w% CB a weak maximum occurred in the frequency region 1 – 10 kHz (Fig.3). We believe that it is mainly due to errors in the measurements at 100 Hz, when the phase often reached the value close to zero and capacity was zero. From the Fig.3 it is also seen that *e*1 for the samples with 2 w% CB is higher in two orders in magnitude.

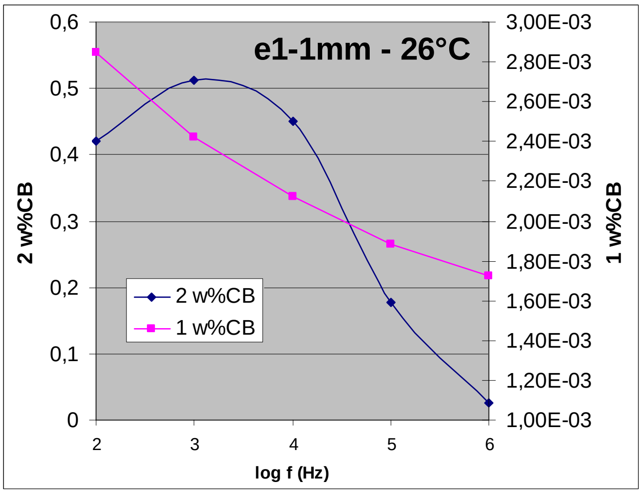

Fig.3. *Dependences of e1 as a function of frequency for the sample on the card with 1 mm sample space at 26 °C at denoted CB concentrations.*

The frequency dependencies of *e*2 showed very low values at higher frequencies and sharp rise frequencies bellow 1 kHz. In double logarithm scale the curves could be fitted with linear functions and consequently the constants *A* and *B* (Eq.4) were evaluated. For the samples with 1 w% CB the constant *B* is close to the value -1,1 to -1,2. On the other hand the constant *B* reaches the values about -1,8 to -1,9 for the samples with 2 w% CB,

All measurements were curried out at the temperature interval 25 – 100 °C. It can be noted that all quantities showed the different values for increasing and for decreasing temperature.

This behaviour is different for the samples with 1 w% CB and the samples with 2 w% CB. In the case 1 w% CB both *e*1 and *e*2 increase for higher temperature and than, when the temperature returns down they decrease but along the lower curve (for *e*1 Fig.4). The increase of e1 can be explain in the term of increase of charge curriers (electrons) mobility in the CB clusters and electron hopping mechanism between the CB agglomerates. On the other hand, the agglomerates are broken by thermal motion of polymer. For *e*2 the curves are in similar shapes. For the samples with 2 w% CB becomes different situation. The built up clusters are destroyed with increasing temperature, therefore *e*1 decreases with increasing temperature (Fig.5).

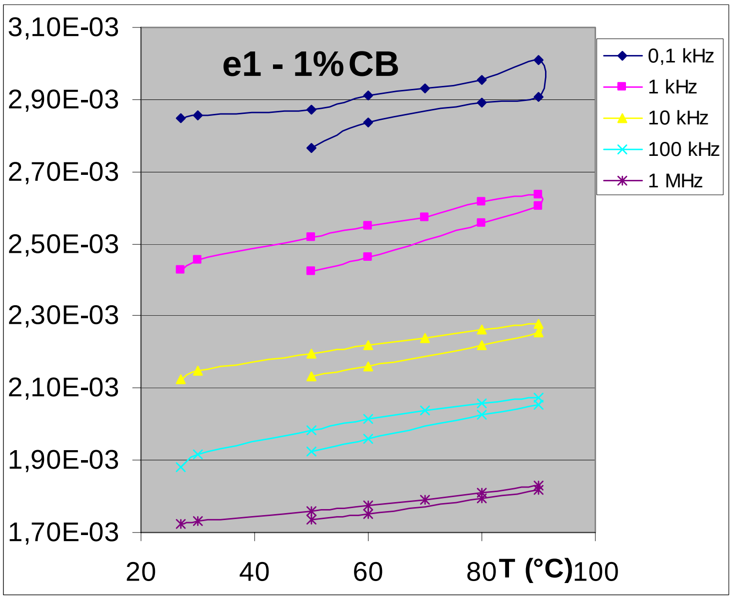

Fig.4. *The temperature dependence of e1 at denoted frequencies for the sample with 1 w% CB.*

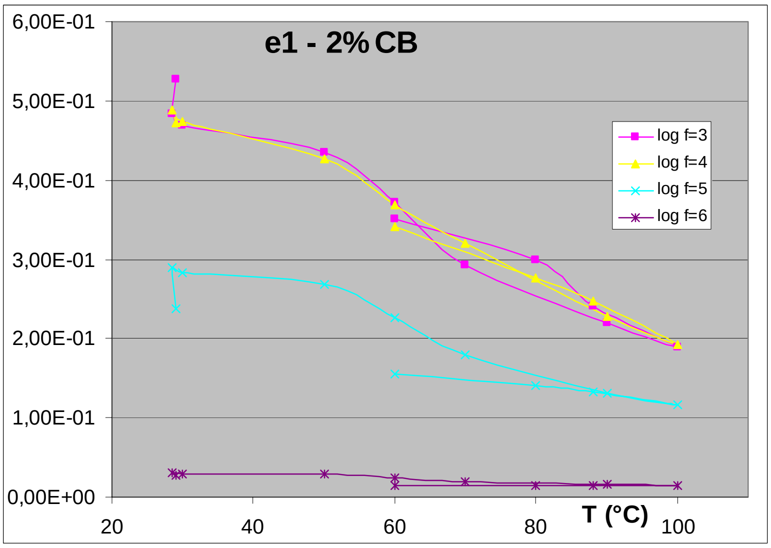

Fig.5. *The temperature dependence of e1 at denoted frequencies for the sample with 2 w% CB.*

Also the constants *A* and *B* are dependent on temperature (Fig.6). The slope of the log e2 vs. log f curve decreases with higher temperature. Constant A which represents the value log (*e*2) at 1 Hz rises with increasing temperature and the curve corresponds to Fig.4.

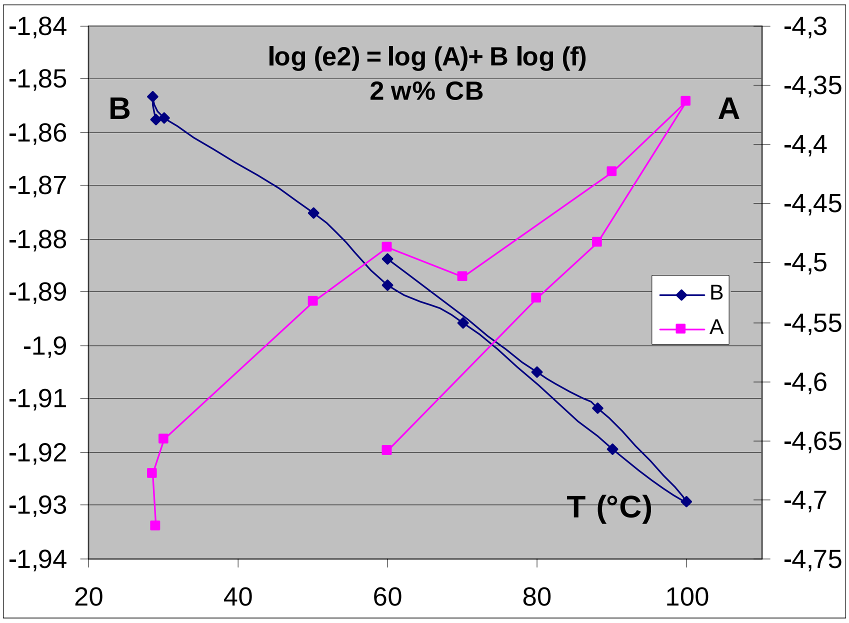

Fig.6. The temperature dependence of the constants A and B in Eq.4 for the sample with 2 w% CB.

When the temperature cycle is repeated both *e*1 and *e*2 in all samples go on decrease but differences between "heating" and "cooling" parts of the curve of one cycle are smaller (Fig.7).

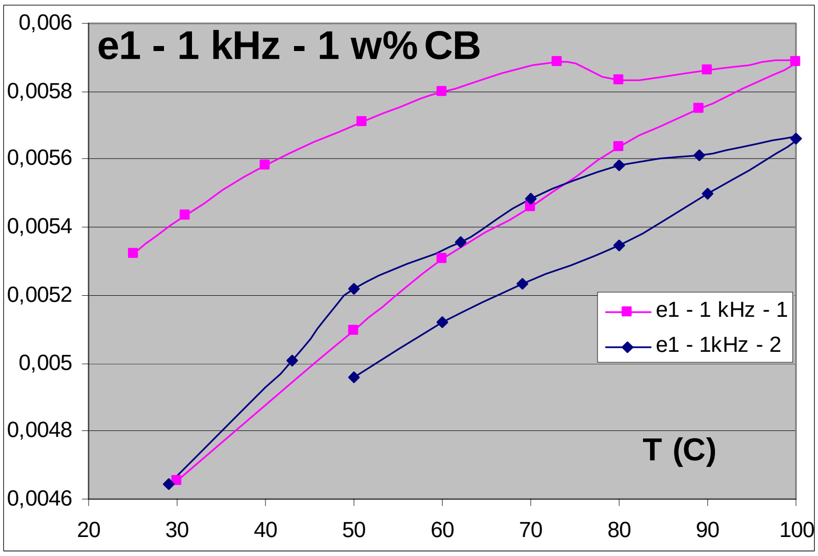

Fig.7. The temperature dependence of e1 of the sample with 1 w% CB in two temperature cycles.

Conclusions

The results of this work can be summarized into following points:

1. The frequency dependencies of both $e1$ and $e2$ show the monotonic decrease without any reasonable extreme.
2. DC conductivity is too small to be able to measure it with HIOKI Hi Tester.
3. The frequency dependencies of $e2$ fulfilled the power law $e2=Af^B$, where A, B are constants. For the samples with lower concentration of CB than percolation, the constant B is closed the 1. For the samples where the conductive properties dominate the constant B falls down to the value -1,8.
4. When $e1$ and $e2$ measured for the increasing and lowering temperature, the hysterezis was observed.
5. Both $e1$ and $e2$ show the higher values when the distance between electrodes is bigger.
6. All results are in qualitatively agreement with dielectric response of composite materials where the main role is played by space charge polarization. Qualitative explanation of our results is based on electron migration in the CB agglomerates which are formed of broken by appropriate viscosity or thermal motion of polymer chains.

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