

STRUCTURE AND DIELECTRICAL PROPERTIES OF COMPOSITES POLYSTYRENE - CARBON BLACK

Jan LIPTÁK, Václav BOUDA

Auhtors: **Jan Lipták, Václav Bouda**
Workplace: **Czech Technical University of Prague, Faculty of Electrical Engineering,
Department of Electrotechnology**
Address: **Technická 2, 166 27 Prague 6, Czech Republic**
E-mail: **liptak@fel.cvut.cz**

Abstract

Properties of carbon black – polymer composites are reasonably affected not only by the carbon black content but also by the distribution or agglomeration of carbon black particles or by the structure of carbon black continuous network. Agglomeration is the result of Van der Waals forces which can be influenced by the present of other substances namely ions. This work deals with optical observations and consequently electrical properties of carbon black – polystyrene composites with modified carbon black. There are differences in the structures and electrical behaviours of the samples with carbon black dried, soaked in water or ethanol and with carbon black with lower ion concentration.

Key words

carbon black – polystyrene composites, modified carbon black , electrical properties

Introduction

When carbon black (CB) is used as a filler in polymer composite, the composite properties can change from insulator to conductive ones. It is widely used for heating cables or screening desks and so on. The composites of conductive polymers with fullerenes are intensively studied for solar cells applications [1].

When the concentration of the filler in the composite reaches the percolation value the continuous electrically conductive network is formed. Dependence of conductivity on CB concentration shows the sharp rise [2] (percolation threshold). Also, the network in the bulk increases the viscosity [3] of the composite. The primary problems of the CB network formation are interactions between CB agglomerates. The interactions can be affected by many parameters.

In summary, it can be pointed out that there are four principal ways to influence the resulting structure of CB in the composite.

1. Effect of polymer [2] - side groups or chains, tacticity, crystalline content, solubility (when the samples are prepared from a solution), thermo-plasticity (if the samples are prepared from a melt), network density (when the structure is fixed in a gel).
2. Effect of external field – electrical [5], [6] (when applied, the CB particles agglomeration is preferred in the direction of the electric field force lines and results to the CB chains (Fig.1)), centrifugal (when the samples are prepared by spin coating method), gravitational (when the sedimentation is possible) and external conditions (temperature, pressure, humidity). The electrical field can induce both polarization of CB-particles with their re-arrangement and/or can induce the change the ionic concentration at the tips of the carbon black agglomerates with the self-assembly of CB-nanoparticles according to the colloidal phase diagram [8].
3. Effect of sample preparation technique – mechanism of pulverisation (mechanical or ultrasonic [7]), the speed and time of dispersion, concentration of added salt.
4. Effect of carbon black [4] (density, surface area, composition).

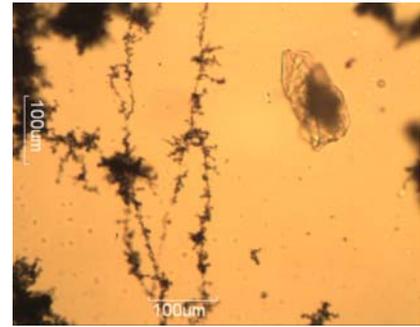


Fig. 1 The affect of the external electric field on CB agglomeration into the chains. The microscope magnification was 800.

The carbon black agglomeration without external field takes place due to Van der Waals forces which are reasonably affected by added or extracted ions or pH value. There are a small amount of different ions inside CB particles or on their surface resulting from the production procedure. From this point of view it seems to be possible to modify CB surface by ion interactions with other ionic substances. We believe that CB ions can be neutralized or extracted. This work deals with the structure and consequently electrical and dielectric properties of carbon black – polystyrene (PS) composites with CB soaked with different substances with ion interactions before dispersing in polystyrene solution.

Experimental

Sample preparation: There are many parameters which affect the composite structure and properties. In this work only three ones were taken into account. 1. The concentration of CB in polystyrene. The samples with CB content from 0.5 to 10 w% were prepared. 2. The thickness of the layer. This represents the total amount of CB per volume in the liquid composite. The higher amount of the liquid composite means a longer time of evaporation and therefore longer time for agglomeration of CB. Four samples of the thickness from 50 to 200 μm were prepared. 3. The dilution of the solution (the concentration of toluene). For optical observation the samples with CB content more than 3 w% had to be prepared from the more diluted solution. For the first preparation the concentration 5 g PS in 75 ml of the solution was used. After the first sample pocket preparation the beaker was filled to 75 ml again. It represents the dilution approximately 2 g per 75 ml of the solution.

THE CONDUCTIVITY OF THE WATER BEFORE (σ_0)
AND AFTER (σ)SOAKING 0.5 g AND 1 g CB FOR TEN DAYS

Table 1

	Sample num.	1	2	3	4	5
	σ_0 (10^{-4} S/m)	1,3	1,3	1,3	1,3	1,3
0,5 g CB	σ (10^{-4} S/m)	74	99	81	70	74
1 g CB	σ (10^{-4} S/m)	85	142	255	130	200

At the first step, 5 g of PS (granulated solid) were mixed with the defined amount of modified or non-modified CB (agglomerated solid). The modification of CB was resulted to four series of the samples. The first series of the samples was prepared from dry (non-modified) CB. The defined mass of CB was kept in the Petri dishes on the hot plate at 120 °C up to the constant weight. The second one was prepared from CB dried by the previous step and soaked in the water vapour. The water content at the equilibrium (constant weight) was about 30 w%. The third one of the samples was soaked in ethanol vapour (the constant weight represents also the concentration about 30 w%). CB of the fourth series was extracted in distilled water for a several days. The water conductivity was measured at the beginning and at the finish of the experiment (Tab.1). From the Tab.1 it is clear that the conductivity of the samples at the finish of the experiment is 10 – 100 times higher than that at the start. It can be explained by the extraction of the ions from the CB particles into water. Other effects as absorption of CO₂ were eliminated by the parallel measurement of the distilled water at the same conditions. Then CB was separated by filtration and dried on the hot plate and mixed with PS.

The dry CB immediately soaks water vapour from air during the CB transport from the hot plate on the analytical balance and to PS. It results to small differences from the weight measured. The weight increase of the dry CB is shown in Fig.2. The similar differences were observed for CB soaked in the water or ethanol vapour. The weight of the samples decreased with the same speed. Therefore, the toluene was immediately added and the solution was formed in approximately 24 – 48 hours. CB agglomerates were sediment. 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 3 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 80°C after ultrasonic homogenisation. Then the liquid composite PS – CB – toluene was coated on the cover glass 18x18 mm on the spin coater and directly into the Petri dishes with diameter 70 mm. After evaporation the plate composites CB – PS with the diameter 45 mm and the thickness from 0,05 mm to 0,2 mm with the CB loading 0,5%w to 10%w were prepared from the dry plates in order to eliminate the non-homogeneous structures on the dish boarder.

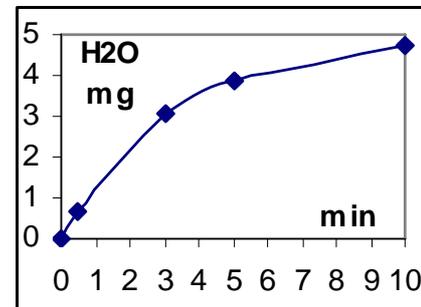


Fig. 2 The amount of water vapor absorbed into 1 g of dry CB as a function of current time

Electrical measurements: The impedance analysis in the frequency region 100 Hz to 1 MHz was carried out with the PM 6306 RLC meter FLUKE with 1 V measurement voltage.

In normal direction the plate condenser with micro shift was used. In planar direction the dot contacts by silver paste of the area about 5 mm^[2] on the boarder of the circle were prepared and the conductance G and the capacity C were evaluated. The diameter of all samples was 45 mm. We made the correction only for the thickness of the samples. From analogy with dielectric measurements the new quantities were defined as follows:

$$\text{For normal direction measurement } \epsilon_2 = \frac{Gd}{f} \quad \text{and} \quad tg = \frac{Gd}{Cf} \quad (1)$$

$$\text{For planar direction measurement } \epsilon_2 = \frac{G}{fd} \quad \text{and} \quad tg = \frac{G}{Cfd}. \quad (2)$$

where f is the measuring frequency, d is the thickness of the plate sample, ϵ_2 is the quantity proportional to the imaginary part of the complex permittivity and tg is proportional to the loss factor $\tan \delta$. Note that the value of capacity is proportional to the real component of the complex permittivity. In our experiments the capacitive component did not play the reasonable role. The results of the measurements in normal and planar directions are not comparable. Exactly, we can compare only the samples with differently modified CB for both methods of measurements. The optical observation was carried out on the microscope RTL with the resolution 100 and 600.

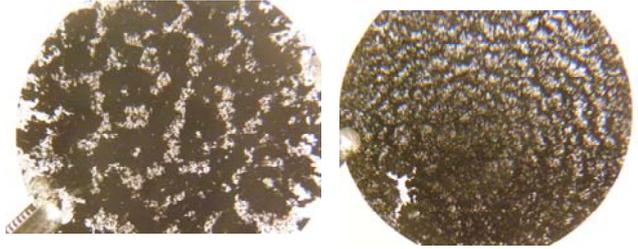


Fig. 3 The macro-snap of the samples with 1 w% CB in PS with a) non-covered and b) with covered Petri dish. The diameter of the circle is 45 mm

Results and discussion

From our sample preparation procedure, it can be pointed out that CB evolves ions when it is soaked in distilled water. The conductivity of the water was measured before and after the soaking. The results for five samples of CB of the amount 0.5 and 1 gram are shown in Tab.1. On the other hand, the increase of the conductivity of toluene or ethanol at the same experiment was not observed.

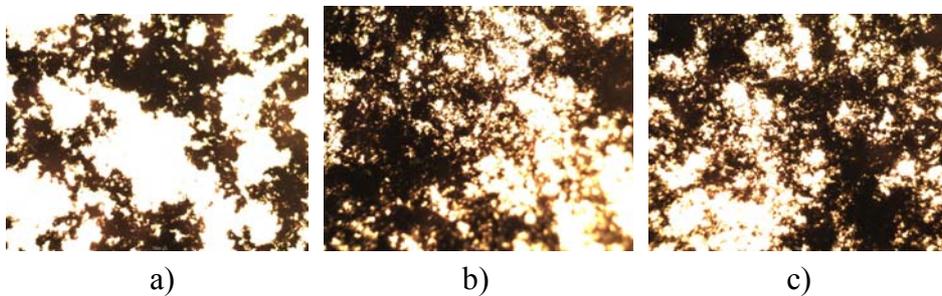


Fig. 4 The structure of 1w% CB network in PS with CB a) dried, b) ions extracted and c) soaked with water. The microscope magnification was 200

Two main results can be pointed out from our optical observation. The final structure of the composite depends on the time (speed) of evaporation. The agglomeration takes place quickly into large agglomerates, when the evaporation time is short. Increasing the time of evaporation (for example by covering the Petri dish or by increasing of toluene content) we observed more fine structure. It can be seen on macro- snaps on Fig.3.

The similar differences in CB agglomeration were observed for the samples with modified CB. The microscope views are shown in Fig.4. Dry CB (Fig.4a) build up the larger and more separated agglomerates. The extracted CB (Fig.4b) is better distributed and therefore they can be expected the better connections between the agglomerates. From the Fig.4c it is clear that there are no visible differences between the network structure of extracted CB and soaked CB with water.

The aim of this work is correlation between the structure and electrical properties. The measurements in alternating field were carried out to be able to register capacitive component too. The impedance measurements show the typical results for partially conductive materials with space charge polarization. Both real and imaginary part of complex permittivity (or modified quantities defined by equations (1) and (2)) for the most samples monotonically decrease with frequency. But there are a few differences between our samples with modified CB. When the plot $\log(\epsilon_2)$ versus $\log(f)$ is linear with the slope minus one, the d.c. conductivity takes place.

From Fig.5 it can be seen that the frequency dependences of ϵ_2 for all samples are close to linear function for the frequencies lower than 10 kHz. The highest conductivity is observed for the de-ionized (extracted) CB and CB soaked in ethanol. The similar linearity is observed for the sample with dry CB, but the conductivity is approx. 10 times lower. It corresponds with different distribution of CB in the polymer matrix (Fig.4). The results of measurements in normal direction are not reasonably influenced by the time of evaporation. On the other hand, the measurement in planar direction depends on time (Fig.6, Fig.7). The time of evaporation was prolonged by covering the Petri dish. For the long time evaporated samples there are no reasonable dependences of ϵ_2 on frequency (Fig.7) and the magnitude of ϵ_2 is 100 times higher than that for the samples evaporated quickly (Fig.6). It can be explained by higher time for agglomeration of CB. It is interesting that in the samples measured in normal direction this effect was not observed. It means that the attractive interactions between the CB particles are preferred in planar direction. On the other hand, the differences between the samples with modified CB are not so high in comparison with the measurements in normal directions (Fig.5). The results for the samples of different thickness were corrected according equations (1) and (2) respectively. For the samples with CB loading higher than 3% the differences modified samples were negligible (Fig.8).

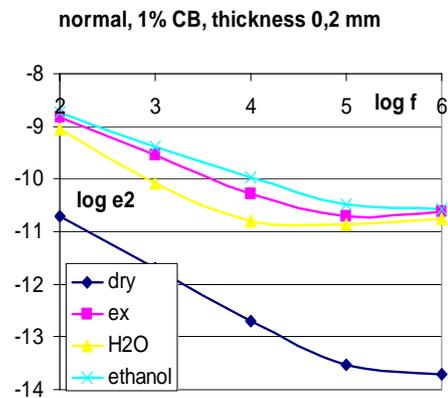


Fig. 5 The frequency dependences of $\log(\epsilon_2)$ for the samples with 1% modified CB. The measurement in normal direction.

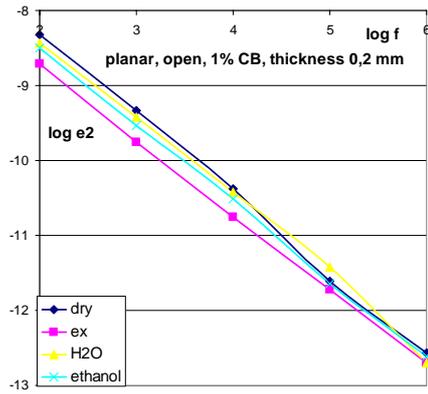


Fig. 6 The frequency dependences of $\log(e_2)$ for the samples with 1% modified CB with open Petri dish. The measurement in planar direction.

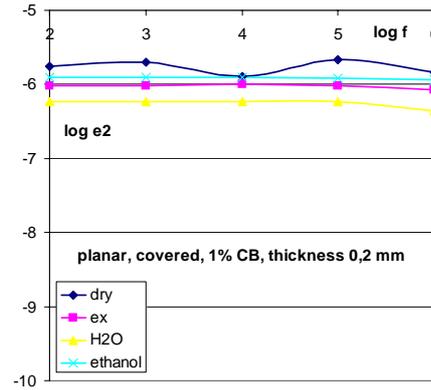


Fig. 7 The frequency dependences of $\log(e_2)$ for the samples with 1% modified CB with covered Petri dish. The measurement in planar direction.

In this paper we have presented the frequency dependences in order we could compare the capacitive and conductive components of the response. It can be pointed out, that the capacitive component was not reasonable for the samples with CB content higher than 1%. Therefore only loss quantity e_2 was presented. The sharp increase between 1% and 3% was observed (Fig.9), when the $\log(e_2)$ is plotted against the CB content. After that, the $\log(e_2)$ increases slower and approximately linearly. Because the increase of $\log(e_2)$ between 1-3% is only two orders in magnitude, we are not sure that the percolation threshold was observed. On the other hand, these results on the layer samples were not presented yet.

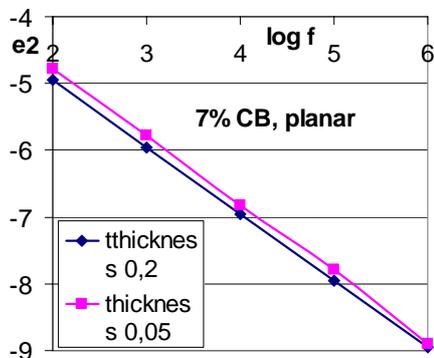


Fig. 8 The frequency dependences of $\log(e_2)$ for the samples with 7% dried CB with the thickness 0,2 and 0,05 mm. The measurement in planar direction.

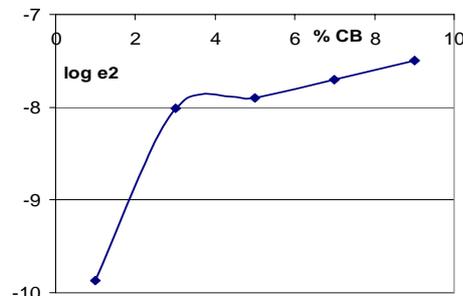


Fig. 9 The dependence of $\log(e_2)$ for the samples with dried CB as a function of CB mass fraction. Planar measurement at 10 kHz.

Conclusions

In this work it was shown that both CB structure and electrical properties of the composites can be changed using the modified CB. Good substances seem to be water and

ethanol with their water bridges. Also, for CB modification can be used the change of ions concentration inside the CB or in CB ion atmosphere. The planar direction agglomeration is preferred for the plane samples and the CB network formation is reasonable influenced by the time of toluene evaporation.

References:

- [1] BJORKLUND, G. S., BAER, T. M.: Photonics Spectra (2007) 70
- [2] MIYASAKA, K. at all: Journal of Materials Science 17 (1982) 1610
- [3] LAKDAWALA, K., SALOVEY, R.: Polymer Engineering and Science, 27 (1987), 1043
- [4] EZQUERRA, T. A. at all.: J. Mater. Sci. Lett, 5, 1065 (1986)
- [5] PRASSE, T. at all: Appl. Phys. Lett., 72, 290-3 (1998)
- [6] LIPTÁK, J.: The 18th joint seminar DMSRE 2.-5.9.2008, Hnanice
- [7] LIPTÁK, J., PILARČÍKOVÁ, I., BOUDA, V.: The 11th joint seminar DMSRE 9.-13.9.2001 Kežmarské Žĺaby
- [8] BOUDA, V.: Mat. Res. Soc. Symp. Proc. Vol. 739, H6.10, p.139-143 © 2003 Materials Research Society, Boston