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# Carbon Nanotubes as Conductive Filler in Segregated Polymer Composites - Electrical Properties

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## 1. Introduction

Carbon nanotubes are of great interest as a filler for polymer composites due to their unique properties such as high electrical and thermal conductivity, ultrahigh mechanical strength, high ratio length/diameter (~1000) at nanosized value of diameter. Several recent reviews summarizing different aspects of the composite investigations display a broad spectrum of properties useful for production of sensitive electrodes, sensors for chemical vapours, electromagnetic radiation shielding materials, electrical heaters, as well as pressure, deformation and temperature sensors and photovoltaic cells (Thostenson et al., 2001; Popov, 2004; Breuer & Sundararaj, 2004; Ramirez, 2005; Moniruzzaman & Winey, 2006; Baibarac & Gomez-Romero, 2006; Rajesh et al., 2009; Spitalsky et al., 2010). More substantially the methods of preparation and properties of CNT based polymer composites are described in new book (Mittal, 2010). Special interest is represented by electrical properties of the composites because of the variety of potential applications.

Such systems are represented in a form of the polymer matrix containing conductive filler creating the conductive network. It seems promising to prepare composite materials with small conductive filler content, which preserves mechanical properties of a polymer along with high electrical conductivity. Random filler distribution typically shows the value of percolation threshold (i.e. critical filler concentration at which a conversion from nonconductive to conductive state occurs) within 10–30% for dispersed metals and 5–15 % for carbon black, for example (Foulger, 1999; Mamunya et al., 2002a). Selectively localized conductive particles in a polymer matrix can form the ordered network of conductive phase creating so-called segregated systems. Considerably lower value of percolation threshold  $\varphi_c$  compared to usual filled polymers can be attained due to this effect, for example (Chan et al., 1997; Bouchet et al., 2000; Mamunya et al., 2002b). On the other hand, high ratio of carbon nanotubes causes lower value of percolation threshold compared to the isotropic filler particles (Simien et al., 2008). Combination of these two factors can lead to the existence of conductivity in the polymer composite at extremely low content of carbon nanotubes.

Segregated polymer composites can be formed either by technological methods in the composites processed by hot compacting or in the polymer blends by filler localization inside one polymer component and on the interface. In this chapter the conditions of creation of the ordered distribution of conductive filler (namely carbon nanotubes) in

polymer matrix and electrical/physical properties of the segregated composites prepared by hot compacting method have been considered and analyzed.

## 2. Development of the segregated system approaches

First such a term “segregated distribution” was proposed in ref. (Malliaris & Turner, 1971) where the authors investigated electrical conductivity of the system based on PE powder and metal (Ni) powder. The scheme of processing of the polymer-metal composite with ordered, segregated distribution of conductive filler is presented in Fig.1. On the first stage of processing the “shells” of small metal particles around randomly distributed large polymer particles are created in the initial mechanical mixture at condition  $D \gg d$ .

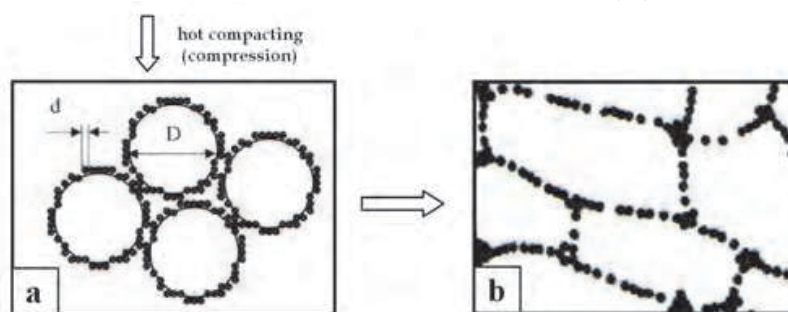


Fig. 1. Scheme of a segregated polymer-filler system processed by hot compacting: a – mechanical mixture of polymer and metal powders,  $D \gg d$ ; b – structure of composite as a result of hot compacting (after Malliaris & Turner, 1971).

After hot compacting (compression at temperature of the polymer softening) the initial distribution of metal particles remains essentially unchanged on the boundaries between polymer grains and forms observed pattern of the segregated structure. While the polymer particles are deformed under pressure and conglomerated creating solid polymer matrix. The Malliaris & Turner model predicts appearance of conductivity (percolation threshold) due to formation of continuous chains of the metallic particle contacts in a monolayer at a volume percent of  $V_a$ . Then further excess of filler leads to the sharp drop of resistivity up to completion of the double layer at  $V_b = 2V_a$ . The  $D/d$  ratio plays a principal role in a structure of conductive phase and a value of percolation threshold. The authors obtained the values of percolation threshold  $V_a$  equal to 14 and 6 % at  $D/d$  ratio 7.5 and 16, respectively, whereas at random distribution of Ni in PE matrix the value of percolation threshold was about 30 %. Decreasing of the polymer particles size  $D$  from 150 to 30  $\mu\text{m}$  (at conductive particles size  $d = 0.8 \mu\text{m}$ ) resulted in increase of  $\varphi_c$  from 5 to 25 % (Bouchet et al., 2000). In composites polytetrafluorethylene/carbon black the value of  $\varphi_c$  was equal to 5 % in case of size of PTFE particles  $D = 1 \mu\text{m}$  while  $\varphi_c = 1$  % if  $D = 100 \mu\text{m}$  (Youngs, 2003).

Evolution of the conductive phase structure as a result of growth of the filler content is shown in Fig. 2. At very low volume filler content  $\varphi \ll \varphi_c$  the condition  $B \gg D$  takes place and distribution of filler can be considered as random in this case (Fig. 2-a). The Fig. 2-b demonstrates noticeable ordered filler structure in the region below percolation threshold,  $\varphi < \varphi_c$ . The pattern of conductive particles which create the infinite conductive cluster at  $\varphi = \varphi_c$  is shown in Fig. 2-c. Further growth of the filler content increases a number of layers of the conductive particles on the interface between polymer particles and forms a conductive skeleton (Fig. 2-d).

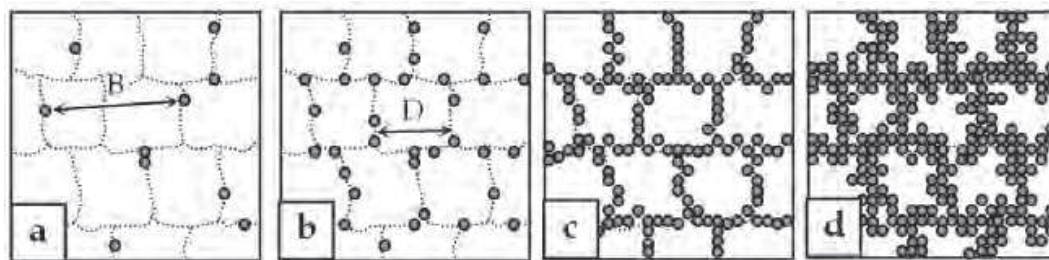


Fig. 2. Scheme of transformation of the segregated structure consisting of conductive particles at volume filler content: a -  $\varphi \ll \varphi_c$ , b -  $\varphi < \varphi_c$ , c -  $\varphi = \varphi_c$ , d -  $\varphi > \varphi_c$ .  $B$  is average distance between filler particles,  $D$  is size of polymer grain.

Such a type of system can be characterized by two values of filler concentration, the average concentration  $\varphi$  related to whole volume of composite and the local concentration of particles  $\varphi_{loc}$  in the wall of formed skeleton. It is clear that  $\varphi_{loc} > \varphi$ . The properties which can be related to the distance between particles and existence of contacts between them, such as electrical and thermal conductivity, dielectric characteristics, certain mechanical parameters are mostly defined by local concentration of filler and shifted to the lower values if the average concentration of filler is used. Thus, in ref. (Kusy and Corneliussen, 1975) it has been found that thermal conductivity in polyvinyl chloride/copper (PVC/Cu) segregated composites more than twice the value was achieved over epoxy/metal composites with only a fraction of loading. The power-law equation, describing the concentration dependence of PVC/Ni segregated system, contains the variable value of exponent in opposite to usual form of this equation with constant value of exponent in case of random filler distribution (Mamunya et al., 2002c). Moreover, it is a reason of low value of percolation threshold  $\varphi_c$  in the segregated systems (average value  $\varphi = \varphi_c$  is lower than true value of  $\varphi_{loc}$  at  $\varphi_c$ ).

Very important for attainable electrical parameters of segregated composites are the conditions of processing. Increasing of mixing time of the powders mixture from 25 to 100 min gives a value of the composites resistivity four orders of magnitude lower due to better distribution of small conductive particles on the surface of polymer particles and breakdown of their aggregates. Increasing of time and pressure of hot compacting promotes the lower values of resistivity as well (Bouchet et al., 2000). In contrast of this, in PE/carbon black composites the pressure did not influence on the composites morphology whereas higher temperature and longer time of pressing led to the penetration of particles of carbon black into polymer grains and increased resistivity of composites (Chan et al., 1997). Mechanical and rheological properties of polymer matrix influence on segregated structure as well. In composites based on methylmethacrylate, butylacrylate and carbon black the value of  $\varphi_c = 1.5\%$  for Young modulus of polymer  $E' = 640$  MPa and  $\varphi_c = 4.9\%$  in case of  $E' = 3.6$  MPa (Kim et al., 2008). The high viscosity of polymer melt minimizes the migration of carbon black particles into PE matrix and deformation of the polymer particles during hot compacting that reduces the value of percolation threshold. From this point of view ultrahigh molecular weight polyethylene (UHMWPE) is a preferred matrix (Zhang et al., 2005).

Since first detailed study of Malliaris & Turner, 1971 many investigations of segregated systems based on metal (and ceramic) particles as conductive filler were fulfilled, for example (Boushet et al., 2000; Bridget et al., 1990; Kusy, 1977; Kusy & Corneliussen, 1975; Lebovka et al., 2006; Mamunya et al., 2002b, 2002c; Privalko et al., 2000; Yacubowicz et al., 1990b). Extensive study of segregated polymer/metal systems and their possible

applications were presented elsewhere (Kusy, 1986) where the prominent achievements in this area have been summarized. The polymer/carbon black composites were thoroughly studied as well (Chan et al., 1997; Chiteme & Mclachlan, 2000; Yacubowicz et al., 1990a; Youngs, 2003; Zhang et al., 2005). Segregated structure of conductive filler was also obtained in emulsions where the particles of conductive filler surround the particles of emulsified polymer (Bridge et al., 1990; Grunlan et al., 2001; Kim et al., 2008; Miriyala et al., 2008). The values of percolation threshold in poly(vinyl acetate)/carbon black composites prepared with using a solution (random distribution of filler) or an emulsion (latex) were 8.18 and 1.2 %, respectively (Miriyala et al., 2008).

A variety of models have been proposed to describe the electrical properties of segregated polymer systems. First model that represented the segregated structure of metal particles in a form of planar hexagonal, square and triangular lattices was not agreed well with experimental values of  $\varphi_c$  and resistivity (Malliaris & Turner, 1971). In ref. (Kusy and Corneliussen, 1975) heightened thermal conductivity in PVC/Ni and PVC/Cu segregated composites was explained by the model of interpenetrating metal/polymer network. Kusy, 1977, has proposed the developed model of distribution of conductive particles on the surface of polymer grains which defined the conditions of continuity of segregated structure created by dispersed metal. Several different models of segregated systems has been analyzed and compared in detail by Lux, 1993, in the extensive review. The parameters of percolation depending on segregated structure and chemical nature as well as size and shape of conductive particles were studied elsewhere (Chiteme & Mclachlan, 2000). Using an approach of non-spherical excluded volume (ellipsoidal shape of the polymer particles after compacting) Youngs, 2003, proposed the equation based on the Bhattacharya model (Bhattacharya et al., 1978). The Bridge et al., 1990, model allows to calculate the number (weight fraction) of colloidal metal particles at maximum latex particle coverage that provides the appearance of conductivity above percolation threshold. Geometrical model of segregated system as 3D shell structure is shown in Fig. 3 and stipulates introduction of the structural coefficient  $K_s = \varphi_{loc}/\varphi$ .

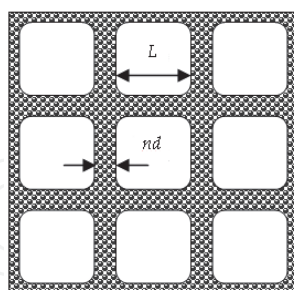


Fig. 3. Geometrical shell structure model. Parameters of the model:  $D=L+nd$ ,  $L$  is size of the excluded volume,  $n$  is the number of layers of conductive particles in the shell.

The geometry of the shell structure model implies:

$$1/K_s = 1 - (1 - nd/D)^3 \quad (1)$$

From this the following expression can be obtained for the percolation threshold  $\varphi_{cs}$  of the shell structure:

$$\varphi_{cs} = \varphi_c [1 - (1 - nd/D)^3] \quad (2)$$

where  $\varphi_c$  is the value of percolation threshold for the randomly distributed filler. This model gives the value of  $\varphi_{cs}$  coincident with the experimental results for PVC/Ni composite at the number of layers of conductive particles  $n=2$ , i.e. every polymer particle is covered with a monolayer of conductive particles. Computer simulation on the base of similar model with the linear size of the system  $N \leq 2048$  in 2D case and  $N \leq 200$  of calculated units in 3D case allowed estimation the value of percolation threshold  $x_c$  in such a manner (Lebovka et al., 2006):

$$x_c = p_c^\infty [1 - (1 + n_{eff}/\lambda)^{-\delta}] \quad (3)$$

where  $p_c^\infty$  is a percolation concentration for the random percolation problem in the infinite system,  $n_{eff}$  is an effective number of the conductive layers ( $n_{eff}/n = 1 + cn^{-k}$ , the  $c$  and  $k$  parameters are different for 2D or 3D systems, i.e. when  $\delta$  is 2 or 3, respectively),  $\lambda = D/d$ ,  $\delta$  is the dimension of system. The equations (2) and (3) give close values of the percolation threshold and satisfactory agreement with the experimental data in PVC/Cu composites.

### 3. Carbon nanotubes in segregated systems

The investigations of segregated systems have got a new impulse with expansion of the carbon nanotubes area, namely as conductive filler in polymer composites. It is caused by possibility to reach still lower value of percolation threshold than for carbon nanotubes and segregated systems separately. Authors (Mierczynska et al., 2004) formed a segregated structure using UHMWPE and single-walled carbon nanotubes (SWCNT) and obtained the value of the percolation threshold equal to 0.5-1.5% depending on type of SWCNT. In next extensive paper the authors (Mierczynska et al., 2007) have shown the influence of CNTs type on the value of  $\varphi_c$ , for example, they found low value of  $\varphi_c = 0.095$  % in case of MWCNT and 0.3-0.7 % for single-walled nanotubes. Big variation of the percolation threshold values was observed for different methods of the segregated systems preparation, thus previous dispersion of CNTs in solvents gave ten times lower value of percolation threshold for the dispersion of SWCNT in DMF versus dry SWCNT. Interesting to note that influence of the processing parameters is similar to that in the segregated systems based on carbon black and metals, namely insignificant influence of pressure and temperature of compacting, and the rise of conductivity with increasing of mixing time of the polymer powder/CNTs mixture. The comparison of CB/UHMWPE and MWCNT/UHMWPE segregated systems has shown that the values of percolation thresholds were less than 0.5 % in both of cases (Hao et al., 2008). Investigation of conductivity of the MWCNT/UHMWPE composites (Gao et al., 2008) has revealed two-dimensional character of the MWCNT structure and low value of percolation threshold ( $\varphi_c = 0.072$  %). In this study the value of critical parameter  $t$  in the scaling relation that describes the conductivity above  $\varphi_c$

$$\sigma = \sigma_0 (\varphi - \varphi_c)^t \quad (4)$$

was equal to 1.15 whereas a theory predicts the value of  $t = 1.6-2$  for 3D conductive structure that is evidence of two-dimensional structure of conductive phase. In ref. (Du et al., 2011) two types of segregated structures based on MWCNT and graphite nanosheets (GNS) formed in HDPE matrix were compared. Lower value of percolation threshold ( $\varphi_c = 0.15$  %) and higher conductivity was revealed in the MWCNT/HDPE composites in comparison with the GNS/HDPE composites ( $\varphi_c = 1$  %).

Introduction of CNTs into polymer emulsions is of benefit to creation of the conductive segregated structure with low value of percolation threshold, for example  $\varphi_c=0.2\%$  in styrene-isoprene emulsion with SWCNT (Ha et al., 2007). The iPP-g-MA nanocomposites, initially artificially brought into a latex form after polymerization, displayed extremely low electrical percolation threshold values of the order of 0.05 % and 0.1 % for SWCNT- and MWCNT-based systems, respectively (Grossiord et al., 2010). The PVA-functionalized CNTs were dispersed in the acrylic latex matrix and obtained nanocomposite films exhibited low optical absorption coefficients. It is expected that this type of nanocomposite coating will potentially exhibit high thermal and electrical conductivity along with high wear-resistance (Vandervorst et al., 2006). A percolation threshold below 0.04% of SWCNT was achieved when an emulsion polymer (i.e., latex) has been used as the polymer matrix (Grunlan et al., 2004). Formation of the segregated SWCNT structure in PVA emulsion allows achievement of high electrical conductivity (48 S/cm) and acceptable thermopower at low thermal conductivity in solid state of the composite that indicates the promising applications of such a type of materials in thermoelectric systems for collection and generation of energy (Yu et al., 2008).

#### 4. Segregated PVC/MWCNT and UHMWPE/MWCNT systems

An excursus in a history of development of the segregated systems indicates that polyvinyl chloride is the most acceptable polymer for creation of segregated composites processed by hot compacting due to its high viscosity, a variety of the powdered PVC types with different size of particles manufactured by industry, wide temperature range of softening (as a result of its amorphous structure) that facilitates a processing (Kusy, 1986). Second attractive polymer is UHMWPE which has very high viscosity, acceptable temperature range of the processing and good mechanical properties.

##### 4.1 The processing features of segregated PVC/MWCNT composites

Electrical, thermal conductivity and dielectric properties of the PVC/MWCNT segregated system depending on concentration of the nanotubes in wide temperature and frequency range have been studied.

Polyvinyl chloride was used in the powder form with average size of particles of 100  $\mu\text{m}$  and density of 1.37 g/cm<sup>3</sup>. Ultrahigh molecular weight polyethylene Hostalen GUR, type GHR 8110, in a powdered form with average size of particles about 100  $\mu\text{m}$  and density of 0.95 g/cm<sup>3</sup> was used. The multiwalled nanotubes were produced by TMSpetsmash (Ukraine) using CVD-method. The MWCNT typically had diameter  $b$  about 12-20 nm and their length  $l$  was about tens of microns ( $\mu\text{m}$ ) that results in the value of aspect ratio  $l/b$  about 1000. Value of the nanotubes density has been taken 2.045 g/cm<sup>3</sup> (Lisunova et. al., 2007). The TEM image of the MWCNT is shown in Fig. 4.

Fig. 5 represents a transformation of PVC/MWCNT structure from mechanical mixture of PVC powder and CNTs (a) to hot compacted segregated composite (c). There is only one distinction compared to Fig.1, namely the presence of intermediate stage (b) that provides the even distribution of tangled CNTs on the surface of polymer grains. It is indispensable condition of the hot compacted system having perfect conductive network without aggregates. In this case one can expect to obtain the conductive composite with low value of the percolation threshold. This has been reached by preliminary solution of MWCNT in ethanol

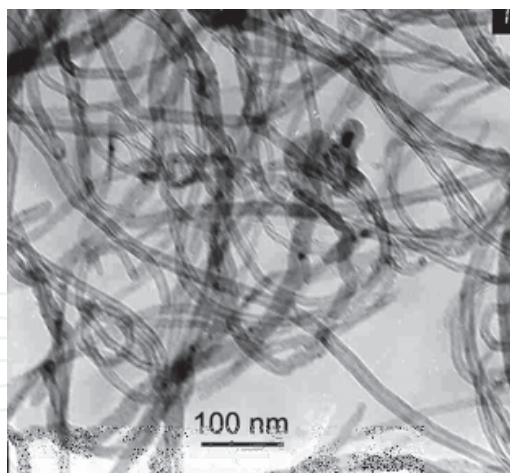


Fig. 4. TEM image of multiwalled carbon nanotubes used for preparation of the composites.

with following exposition during 20 min under ultrasonic action with frequency of 22 kHz. The sonicated MWCNT and PVC powder were homogenized by thorough grinding in a porcelain mortar to the visually homogeneous state. Homogenized composite was placed into a hot steel mold heated to 145 °C and then pressed (hot compacted) during 5 min at 20 MPa with subsequent cooling of the mold in the air flow to room temperature. The samples of pressed composites used for dielectric and electrical measurements were produced as discs with 30 mm diameter and 1-1.5 mm height.

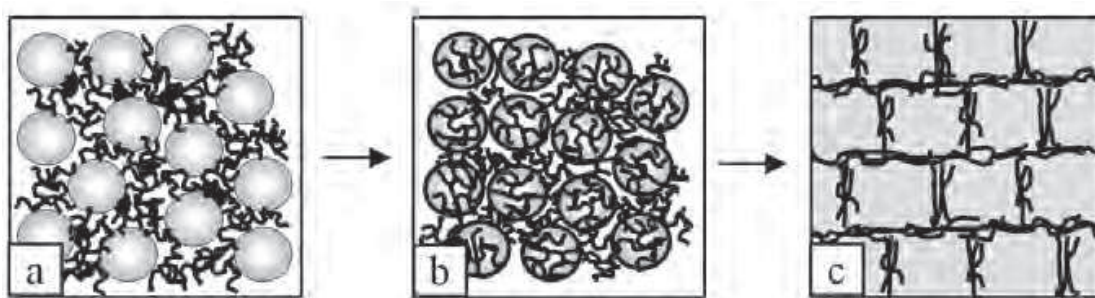


Fig. 5. A model of evolution of the PVC/MWCNT structure along a process of its forming by hot compacting method

The DC electrical conductivity was measured using a two-contact scheme. The values of DC conductivity  $\sigma_{DC}$  (S/cm) were estimated using the following equation:

$$\sigma = \frac{h}{R \cdot S} \quad (5)$$

where  $R$  (Ohm) is an electrical resistance measured experimentally using E6-13 teraohmmeter, and  $h$  (cm) and  $S$  (cm<sup>2</sup>) are the thickness and area of the sample, respectively. The characterization of the dielectric parameters of the samples, such as real  $\epsilon'$  part of the dielectric permittivity and AC conductivity  $\sigma_{AC}$ , were determined by means of the Novocontrol system in the frequency range from 10<sup>-1</sup> Hz to 10<sup>6</sup> Hz at room temperature. Thermal conductivity was measured by method described in (Boudenne et al., 2004). The structure of nanotubes was examined using transmission electron microscope (TEM) Philips

CM120. The investigations of structure of the PVC/MWCNT composites were fulfilled using the scanning electron microscope (SEM) Hitachi S800 and the optical microscope Carl Zeiss Primo Star.

#### 4.2 Structure of segregated PVC/MWCNT system

The structure of hot compacted PVC/MWCNT system was studied by optical and electron (SEM) microscopy. Figs. 6 and 7 display the segregated structure of composites. Optical microscope images of the segregated PVC/MWCNT structure are presented in Fig. 6. It shows the evolution of the composite structure along increase of the MWCNT concentration from 0.02 % that is below percolation threshold  $\phi_c$  (Fig. 6-a) through 0.04 % (close to  $\phi_c$ ) (Fig. 6-b) to 0.07 % (above  $\phi_c$ ) (Fig. 6-c). One can see more pronounced boundaries between polymer grains, blackened by nanotubes, with increase of the MWCNT content that reflects a creation of the nanotubes framework.

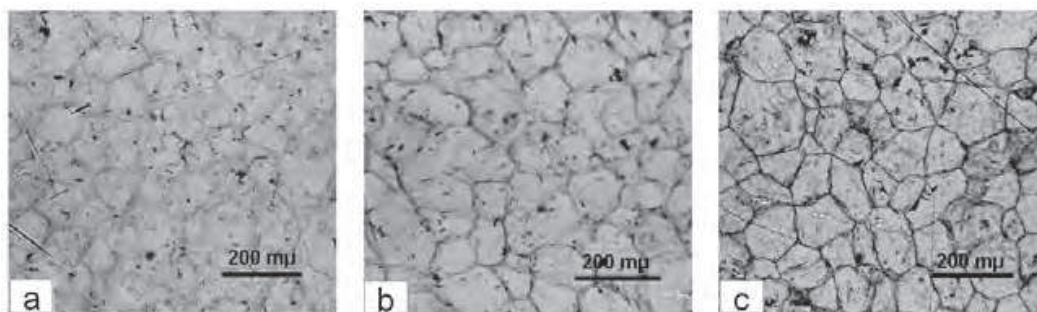


Fig. 6. Optical microscope images of segregated PVC/MWCNT composites with the MCWNT content: a - below (0.02%), b - close (0.04%) and c - above (0.07%) percolation threshold.

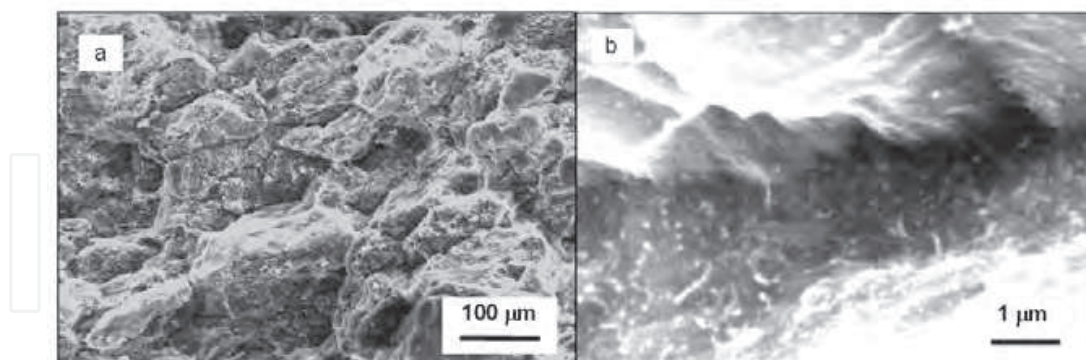


Fig. 7. SEM image of the PVC/MWCNT composite after cryogenic fracture: a – hot compacted composite, b – intergrain surface in the composite.

Hot pressing deforms polymer particles and results in formation of compacted continuous polymer phase, where conductive paths of CNTs are located on the boundaries between particles. Fig. 7 demonstrates the SEM images of PVC/MWCNT composite prepared by the fracture in liquid nitrogen. It is seen a granular structure of the polymer matrix with granules covered by nanotubes (Fig. 7-a). The presence of nanotubes on the surface between grains displays Fig. 7-b.

### 4.3 Electrical properties of segregated PVC/MWCNT composites

The concentration dependence of DC conductivity  $\sigma$  of the PVC/MWCNT composites is represented in Fig. 8. The electrical conductivity of composites abruptly increases by many orders of magnitude when the filler content  $\varphi$  exceeds the threshold concentration  $\varphi_c$ . It can be seen that the non-conducting - conducting state transition takes place at a rather small volume content of MWCNT, approximately equal to 0.05 vol. %. The electrical conductivity behavior above the percolation threshold can be described by the equation (4). In this equation the critical exponent  $t$  reflects dimensionality of the system and universality class of the problem (Stauffer & Aharony, 1992),  $\sigma_0$  is an adjustable parameter. The theoretical random percolation value  $t$  is close to 2.0 for the three-dimensional system.

Insertion to Fig. 8 shows scaling of  $\sigma$  versus  $\varphi - \varphi_c$  in the double logarithmic presentation. Line corresponds to the least square fitting of the experimental data with  $\varphi_c = 0.00047$ . The slope of this line gives  $t = 3.3$ ; this value exceeds the theoretically predicted value  $t \approx 2.0$ . This effect can be explained by non-statistical ordered distribution of conductive phase in the polymer matrix since value  $t \approx 2$  is provided by random (statistical) distribution of conductive particles in non-conductive medium (Stauffer & Aharony, 1992). As it is seen in Fig. 8, dependence of electrical conductivity on the content of nanotubes in PVC/MWCNT composites demonstrates very low value of the percolation threshold  $\varphi_c = 0.00047$  ( $\approx 0.05$  vol. %). The high anisotropy of the MWCNT with aspect ratio  $l/b \approx 1000$  is one of the reasons of such effect. Higher aspect ratio of the filler particles leads to lower value of the percolation threshold (He & Ekere, 2004).

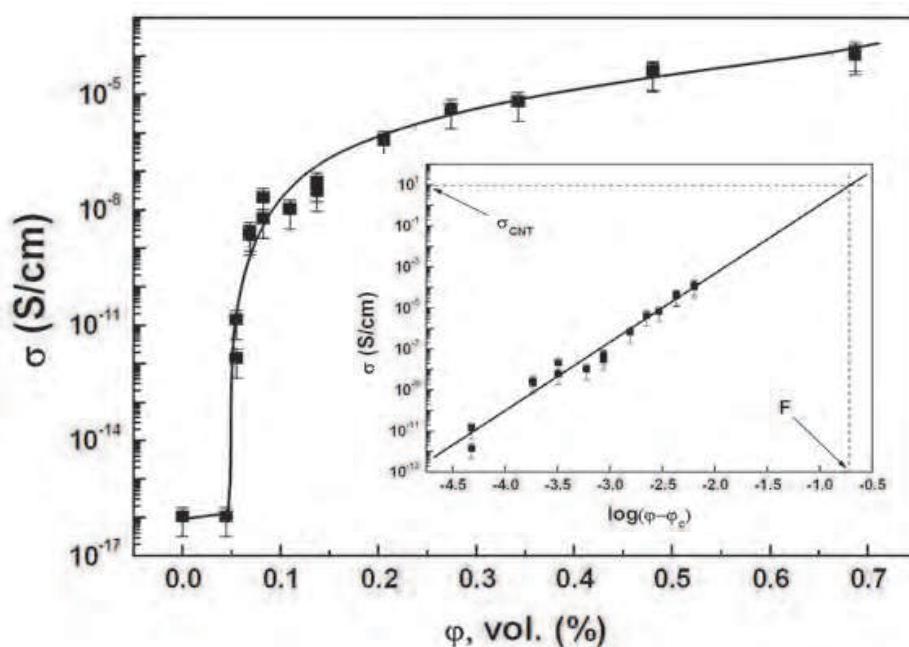


Fig. 8. Electrical conductivity  $\sigma$  versus volume content  $\varphi$  of nanotubes. The insertion presents the scaling relation  $\log \sigma \sim \log (\varphi - \varphi_c)$  to fit the values of  $\varphi_c$ ,  $t$  and  $\sigma_0$ .

The  $\log \sigma \sim \log (\varphi - \varphi_c)$  function, used for calculation of  $t$  value enables to define the value of the packing-factor  $F$  or a limit of the composite filling for the given type of the filler. Extrapolation of this function to  $\sigma_f$  equal to 10.0 S/cm (*i.e.* to the conductivity of MWCNT) gives us the value of  $\varphi = F$  (insertion in Fig. 8). The value of  $\sigma_f = 10.0$  S/cm was obtained

using a method of the fillers conductivity measurement described in ref. (Mamunya et al, 2004). The  $F$  parameter is a limit of the system filling and it is equal to the highest possible volume fraction of the filler:

$$F = \frac{V_f}{V_f + V_p} \quad (6)$$

where  $V_f$  is the volume occupied by the filler particles at the highest possible filler fraction,  $V_p$  is the volume occupied by the polymer (space among filler particles). The value of  $F$  depends on the shape of particles and their type of spatial distribution. For statistically packed monodispersed spherical particles of any size, the  $F$  value is equal to 0.64. In case of deviation of the shape of particles from the spherical one or presence of nonstatistical ordered (shell or skeleton) structure, the  $F$  value decreases with  $V_p$  increasing. The use of polydispersed filler particles results in increase of  $F$  (Kusy, 1977). Thus,  $F$  value characterizes the filler phase topology taking into account the shape, fractional size and spatial distribution of particles. The volume fraction  $F$  value, defined in such a way, is equal to 0.20 (insertion in Fig. 8). It means that the volume fraction of the MWCNT filler in a polymer can not exceed 0.20, and at  $\phi=0.20$  the composite has conductivity equal to the conductivity of the filler:  $\sigma_f = \sigma_{CNT}$ .

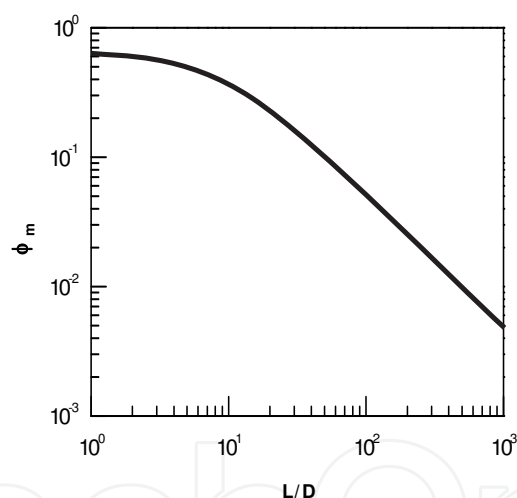


Fig. 9. The values of packing-factor versus a filler aspect ratio for its random distribution (after Bigg, 1995). Here  $\phi_m = F$ ,  $L/D = l/b$ .

The value of  $F$  for nanotubes is essentially lower than 0.64 because of anisotropic shape of the MWCNT particles, as far as their high aspect ratio  $l/b$  causes their loose packing. For aligned MWCNT particles, the value of  $l/b \approx 1000$ . However, as MWCNT are tangled, the value of  $l/b$  has to be lower. It can be estimated from the computer simulation of the packing-factor  $F$  versus  $l/b$ , given in (Big, 1995) (Fig. 9). This plot can be described by empirical equation which relates the values of  $F$  and  $l/b$  (Lisunova et al., 2007):

$$F = \frac{5}{\frac{75}{10 + a} + a} \quad (7)$$

where  $a=l/b$  (in case of very high aspect ratio  $a$  ( $a \gg 1$ ) this relation can be rewritten as  $F \approx 5/a$ ). Using the value of  $F=0.20$ , the eq. (7) gives  $a=22$ . Taking into account that the value of  $b$  for the MWCNT used is in the range of 10-20 nm, we can accept the average  $b$  value equal to 15 nm, which gives  $l = 330$  nm. This value may be defined as an effective nanotube size  $l = l_e$  and may be associated with the average distance between linkages of crossing nanotubes; i.e.  $l_e$  means the length of a nanotube between adjacent contact linkages with other nanotubes. Fig 4 demonstrates that this value is quite realistic.

Described above models (see section 2) predict decrease of the percolation threshold  $\varphi_{cs}$  in a segregated system compared with the value of  $\varphi_c$  for random distribution of conductive filler in the polymer matrix. The value of  $\varphi_{cs}$  depends on the  $D/d$  ratio under condition of  $D \gg d$ , where  $D$  is size of the polymer grains ( $D=100 \mu\text{m}$  for the PVC used) and  $d$  is size of the filler particles. It can be determined that the value of  $d$  is equivalent to the effective size of a nanotube, i.e.  $d = l_e$ . In a segregated polymer/MWCNT system, the value of the percolation threshold can be calculated as (Lisunova et al., 2007):

$$\varphi_{cs} \approx \frac{3n}{\frac{l}{b} \cdot \frac{D}{d}} \quad (8)$$

where  $n$  is the number of layers of the filler on the boundary between polymer grains, and it is rather small:  $n \sim 1$ . Taking into account that  $l = l_e$  and  $d = l_e$ . ( $l_e = 330$  nm), the value of  $\varphi_{cs}$  can be estimated by eq. (8). Such a calculation gives  $\varphi_{cs} \approx 4.5 \cdot 10^{-4}$ . The experimentally measured value of  $\varphi_c$  in the PVC/MWCNT composites is  $4.7 \cdot 10^{-4}$ , which is in excellent agreement with the theoretically estimated value of  $\varphi_{cs}$ . It follows from the said data that the observed ultra-low value of the percolation threshold  $\varphi_c$  in the PVC/MWCNT composites can be explained by both very high aspect ratio of the nanotubes and segregation of MWCNT inside the PVC matrix.

Temperature dependencies of conductivity of the PVC/MCWNT composites are shown in Fig. 10. The increase of filler content changes the form of the curves. In pure PVC and composite with 0.04 % MCWNT the conductivity increases with rise of temperature (curves 1, 2). Therefore it is possible to assume ionic character of conductivity in these systems as a growing of conductivity with temperature is the feature of ionic conductivity and is caused by rise of the ionic mobility (Margolis, 1989; Blythe & Bloor, 2005;). The temperature dependence is found to be composed of two linear regions with a bend at temperature of glass transition  $T_g$ . The transition from glassy state to high-elastic state leads to stronger dependence of conductivity on temperature that can be related to lightened ionic mobility in the polymer state with heightened molecular mobility. These dependencies are represented by Arrhenius plot in Fig. 11:

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right) \quad (9)$$

where  $E$  is an activation energy,  $k$  is a Boltzmann constant. Calculation of the activation energy values for the both parts of curve gives the  $E$  values in the temperature regions higher and lower of  $T_g$  respectively: 23.0 and 2.1 kcal/mole for the pure PVC and 19.0 and 0.9 kcal/mole for the PVC/MWCNT composite with 0.04 % MWCNT.

Crossing glass transition temperature the value of activation energy sharply increases as a result of rise of the charge carrier mobility at temperature higher of  $T_g$ . Such values of the

activation energy are typical for ionic conductivity, for example the close values of  $E$  (22.0 and 3.6 kcal/mole) were found in the PVA/ $H_3PO_4$  system (Margolis, 1989). Influence of temperature (temperature higher or lower of  $T_g$ ) on the value of activation energy enables to include the segmental mobility in the charge transport process. This approach takes into consideration the change of viscosity of the polymer matrix under temperature action that, in turn, influences on the charge carriers mobility (Seanor, 1982).

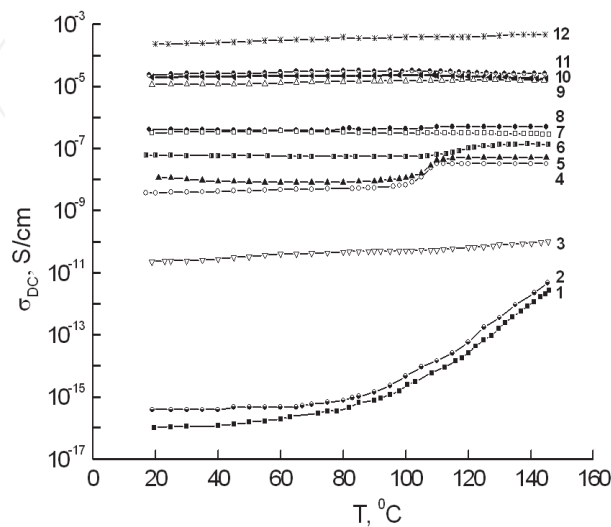


Fig. 10. Temperature dependencies of conductivity for composites with different content of filler. Content of MWCNT in the composites (vol. %): 1 – 0, 2 – 0.044, 3 – 0.054, 4 – 0.08, 5 – 0.107, 6 – 0.134, 7 – 0.201, 8 – 0.268, 9 – 0.336, 10 – 0.470, 11 – 0.672, 12 – MWCNT.

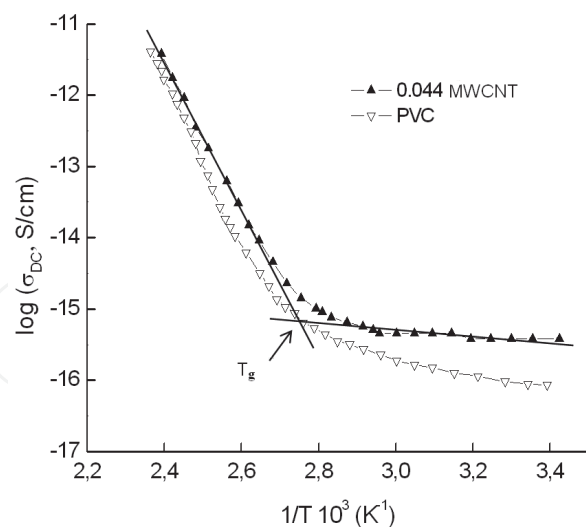


Fig. 11. Arrhenius plots for the conductivity of the pure PVC and composite with 0.044 % of MWCNT.

Even insignificant excess of the filler concentration over percolation threshold leads to the change of the conductivity character, thus at MWCNT content equal to 0.054 % the conductivity  $\sigma$  increases essentially and becomes almost independent on temperature (Fig. 10, curve 3). It indicates a conversion from ionic conductivity through the matrix to electronic

type of conductivity through the filler phase. Further growth of filler content causes the increase of the conductivity value and it becomes independent on temperature in the region of 20-150 °C (curves 4-11). Only the composites with MWCNT content from 0.08 to 0.134 % (curves 4-6) show weak shift of conductivity in the region 100-120 °C that is essentially higher of  $T_g$ . Measurement of the nanotubes conductivity demonstrates independence of  $\sigma$  on temperature (curve 12), accordingly temperature dependence of conductivity of PVC/MWNT composites has the same character since it is provided by conductivity of the filler phase.

4.4 Dielectric properties of PVC/MWCNT and UHMWPE/MWCNT systems

Fig. 12 represents dielectric constant  $\varepsilon'$  and AC conductivity  $\sigma_{AC}$  versus frequency. The value of  $\varepsilon'$  in the PVC/MWCNT composites with the MCWNT content 0–0.04 vol. % (i.e. lower than percolation threshold) are close and independent on frequency. This value of  $\varepsilon'$  increases and reveals a negative slope if the filler content exceeds the percolation threshold. The frequency dependence of dielectric parameters in two-phase conductive-insulating system can be considered with two models, such as intercluster polarization (IP) that implies polarization effects between clusters inside percolation system or anomalous diffusion (AD) within cluster (Song et al., 1986; Yoon & Lee, 1990; Youm & Lee, 1991). The IP model predicts the power-law dependence of  $\varepsilon'$  and  $\sigma_{AC}$  on the frequency that may be written as follows:

$$\varepsilon'(\omega) \propto \omega^{-y}$$
 (10)

$$\sigma(\omega) \propto \omega^x$$
 (11)

$$x + y = 1$$
 (12)

where  $y = s/(t + s)$  and  $x = t/(t + s)$ . The critical exponents,  $x$  and  $y$ , have to satisfy the condition (12). In the case of three-dimensional lattice the critical exponents  $t$  and  $s$  are:  $t \approx 2$ ,  $s \approx 0.8$  (Stauffer & Aharony, 1992) that gives the values of  $x$  and  $y$  equal to 0.72 and 0.28 respectively.

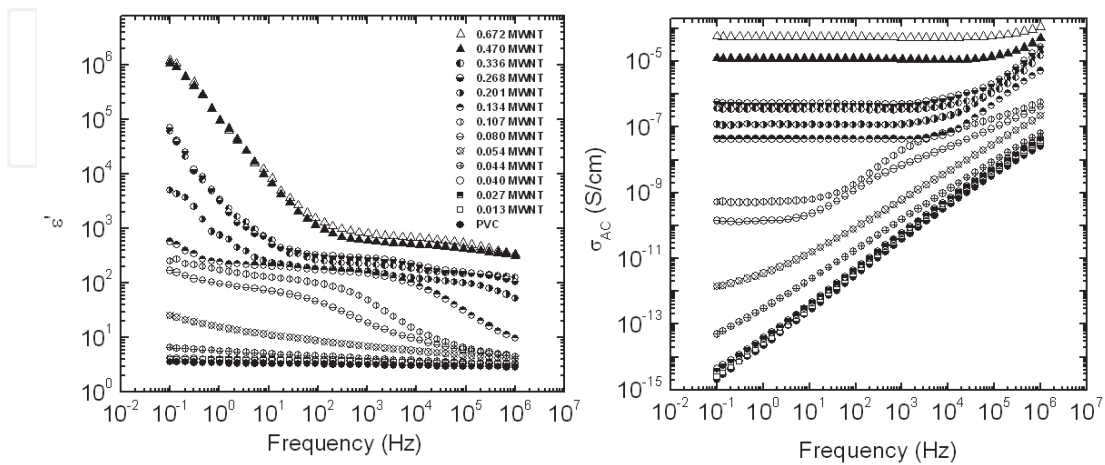


Fig. 12. Frequency dependencies of dielectric constant  $\varepsilon'$ , and AC conductivity  $\sigma_{AC}$  for the composites with different MWNT content.

In the AD model the values of  $x$  and  $y$  are equal to 0.58 and 0.42 respectively for three dimensions. For the conductive PVC/MWCNT composites with MWCNT content in the range of 0.08–0.134 % the average value of  $y$  (calculated for the  $10^{-1}$ – $10^2$  Hz frequency range) is found to be 0.18, which is lower than the theoretically predicted value.

Plot of conductivity versus frequency in a double logarithmic scale (Fig. 12) shows two cases of the frequency dependence of AC conductivity  $\sigma_{AC}$ : (a) below percolation threshold the values of  $\sigma_{AC}$  of the composites are overlapping and the curves have average slope close to 1, which indicates the highly insulating material (McLachlan et al., 2005); (b) above  $\varphi_c$  the conductivity is constant at low frequency due to contribution of DC conductivity. The average slope of curves at higher frequencies is 0.91 that exceeds the theoretically predicted value of critical exponent  $x=0.72$ . One can consider satisfactory fulfilling the general scaling relation (10), the measured values are  $x+y=1.09$ . Thus the experimental results are closer to the IP model than to the AD model. Note that in (Song et al., 1986; Yoon & Lee, 1990; Youm & Lee, 1991) the critical exponents  $x$  and  $y$  do not agree separately with the theoretical predictions but general scaling law (10) is satisfactorily fulfilled. For PE/MWCNT composites the authors (Liang & Tjong, 2006) have found an agreement of the experimental values of critical exponents with the theoretical prediction by power law relations (10)–(12). For higher concentration of the filler in the composites (in the range of 0.201–0.672%) the values of  $\varepsilon'$  grow drastically. The reason of such an effect can be an electrode polarization that leads to a separation of charges which gives an additional contribution to the polarization. It occurs for moderately to highly conductive systems and results in extremely high values of the real and imaginary part of the complex dielectric permittivity (Kremer & Schonhals, 2003). In fact Fig. 12 demonstrates the presence of very high  $\varepsilon'$  values equal to  $10^5$ – $10^6$  in the range of low frequencies  $10^{-1}$ – $10^0$  Hz for the samples with filler concentration above 0.201%.

The comparison of conductivity and dielectric parameters ( $\varepsilon'$  and  $\tan \delta$ ) versus MWCNT content in PVC/MWCNT and UHMWPE/MWCNT segregated systems is presented in Fig. 13. Dependence of electrical conductivity on the nanotubes content in the PVC/MWCNT and UHMWPE/MWCNT composites demonstrates very low values of the percolation threshold, equal to 0.00047 ( $\approx 0.05$  vol. %) and 0.00036 ( $\approx 0.04$  vol. %), respectively. It is a result both, of high anisotropy of MWCNT with aspect ratio length/diameter  $\approx 1000$  and of segregated distribution of CNT in the polymer matrix. It is interesting that the  $\varphi_c$  value is lower for UHMWPE/MWCNT composite although the geometrical parameters for both of composites are identical.

Dielectric characteristics, measured at fixed frequency 1 kHz, demonstrate the percolation behaviour as well (Fig. 13). In the region above percolation threshold  $\varphi_c$  the sharp increase of  $\varepsilon'$  and  $\tan \delta$  takes place, after that the values of dielectric parameters reach the plateau. Such behavior is predicted by model for two-phase insulating/conducting systems and was observed in polymer/dispersed metal composites (Mamunya et al., 2002c). Rise of  $\varepsilon'$  in the region above percolation threshold was observed for the LDPE/MWCNT composites in (Liang & Tjong, 2006). It is necessary to note that some differences for PVC/MWCNT and UHMWPE/MWCNT composites exist. The value of  $\varepsilon'$  on the plateau is an order of magnitude higher for UHMWPE/MWCNT than for PVC/MWCNT. Probably it is caused by heightened conductivity of UHMWPE/MWCNT composite which is ten times higher than in PVC/MWCNT composite for samples with maximal content of MWCNT. The reason of such features is not clear since the geometry of conductive phase (the values of  $D$  and ratio  $D/d$ ) is the same for both of composites.

It is seen from Fig. 13 that the interval of  $\tan \delta$  alteration with change of MWCNT content is much wider for UHMWPE/MWCNT composites. The maximal values of  $\tan \delta$  are approximately equal for both of composites while initial value of  $\tan \delta$  for UHMWPE is two orders of magnitude lower than for PVC. It is known that polyethylene is a polymer with one of lowest values of dielectric losses. Very small content of carbon nanotubes that is slightly higher of the  $\varphi_c$  value leads to sharp increase of dielectric losses. Probably it can be caused by creation of segregated structure of CNT in the volume of hot compacted composite that forms "shielding framework" of conductive phase for the electromagnetic flow. Such ability is promising for creation of shielding materials for electromagnetic irradiation.

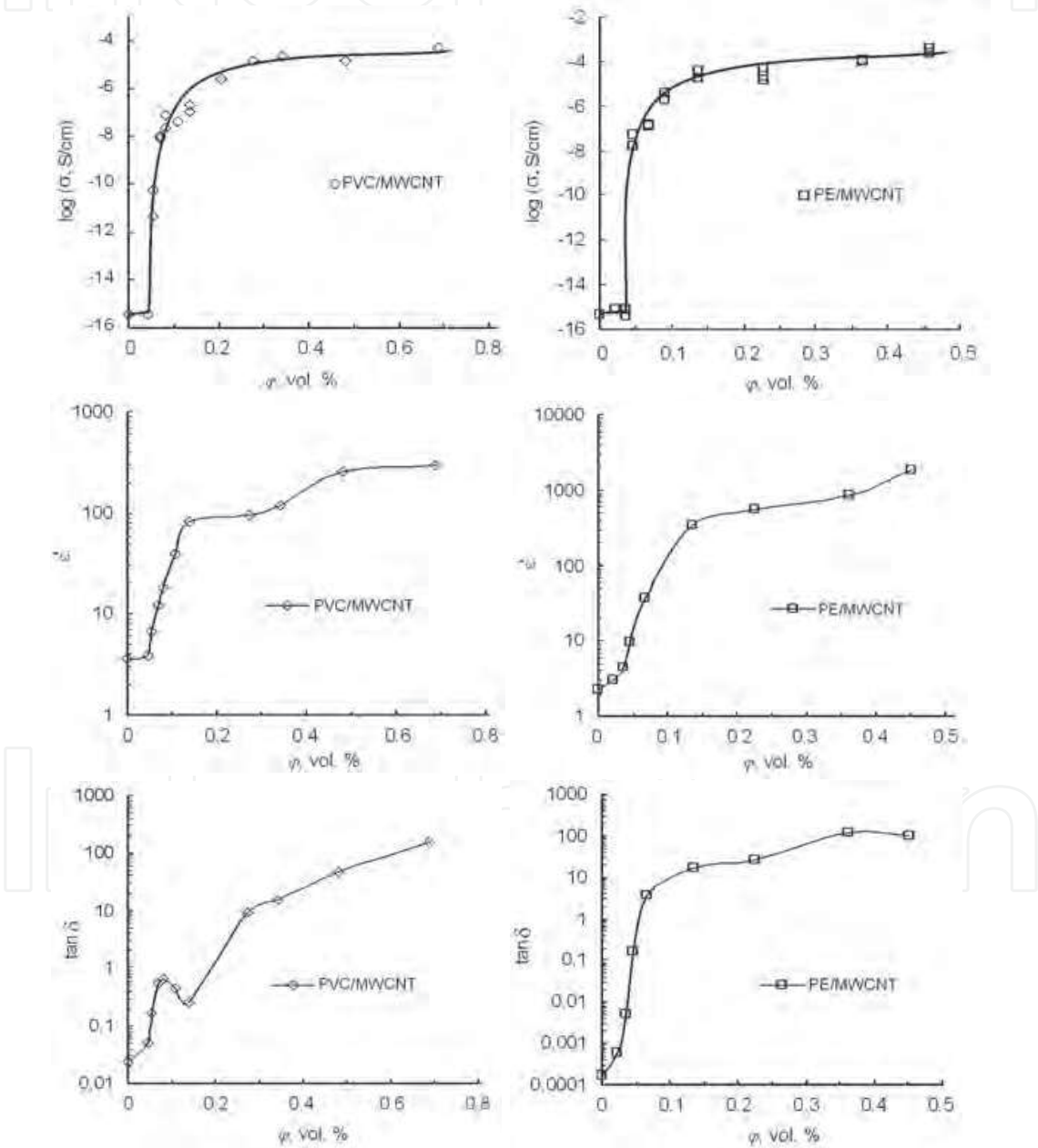


Fig. 13. Dependence of conductivity  $\sigma$ , dielectric constant  $\epsilon'$  and loss-factor  $\tan \delta$  on MWCNT content for the PVC/MWCNT and UHMWPE/MWCNT composites.

A very low concentration of MWCNT in the composites and a specific type of their distribution as the segregated nanotube shell structure remains most part of the polymer in the neat state within framework. Consequently, one could expect the dielectric properties of polymer/MWCNT composites close to those ones in the unfilled polymer. However, the experimental data reveal very high contribution of conductive phase in the dielectric response. We can assume that majority of nanotubes creating the framework takes part in conductivity due to their high local concentration  $\varphi_{loc}$  in the shell whereas in usual statistical conductive clusters only small part of particles creates a conductive skeleton (Feder, 1988), and the rest ones are dead ends and non-conductive side branches.

#### 4.5 Thermal conductivity of PVC/MWCNT composites

The thermal conductivity values of PVC/MWCNT composites and their associated uncertainties are plotted in Fig. 13 versus MWCNT volume content  $\varphi$ . The variation of  $k$  can be separated into three regions. For very low concentrations ( $\varphi < 0.05$  vol. %), we observe a drop of the thermal conductivity. This decrease of  $k$  represents about 6 % of the thermal conductivity of the PVC matrix. Then, for concentrations  $0.05 < \varphi < 0.14$  vol. %, a rapid increase of the thermal conductivity is observed. Finally, for the highest concentrations ( $\varphi > 0.14$  vol. %), the thermal conductivity increases linearly upon the MWCNT volume fraction. Dependence of the thermal conductivity  $k$  on the volume content of filler is not monotonous and reaches a minimum at  $\varphi \approx 0.05$  vol. %, which coincides with the percolation threshold value  $\varphi_c$ . However, in our opinion, creation of an infinite conductive cluster of fillers at  $\varphi = \varphi_c$  can not be a reason for decrease of the thermal conductivity values. The progressive introduction of filler into the polymer matrix is accompanied by two opposite effects influencing heat transport in the composite. First is appearance of a surface of a new phase and, correspondingly, of an interfacial layer, in which the phonon scattering tends to reduce

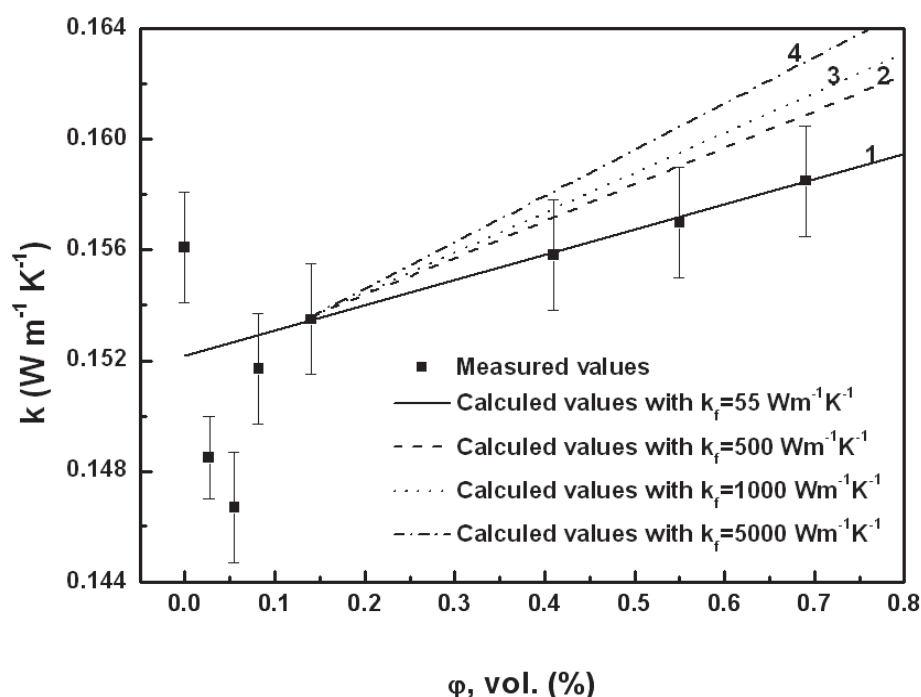


Fig. 13. Thermal conductivity of composites as a function of MWCNT concentration. Lines are calculated in accordance with eq. (13).

the heat flow transport, thus resulting in the interfacial resistance. Second effect is the presence of the volume of a new phase with high thermal conductivity, which results in increase of the heat flow. Our results (Fig. 13) demonstrate that the first effect is predominant at low filler concentrations ( $\varphi < \varphi_c$ ). Then, increase of the MWCNT content at  $\varphi > \varphi_c$  leads to prevalence of the second effect, and we can observe increase of the thermal conductivity due to additional heat transfer through the filler phase (Mamunya et al., 2008). Indeed, in spite of a small content of filler in the polymer matrix at  $\varphi < \varphi_c$ , the presence of the filler can noticeably influence the heat transport owing to high specific surface of the CNTs ( $\sim 190 \text{ m}^2/\text{g}$ ). As it was shown in (Mamunya et al., 2002b; Lebovka et al., 2006), conductive behaviour appears at  $\varphi = \varphi_c$  in the segregated system, where each polymer particle is covered by one layer of filler particles and even not full covering is possible (Kusy, 1977). In this model, the filler creates a shell inside the polymer matrix with thickness of one filler particle. In our case, according to this model, the MWCNT are forming a "shielding framework" with developed surface for the heat flow at  $\varphi < \varphi_c$ , which transforms into "conductive framework" at  $\varphi = \varphi_c$ . Thus, the presence of a segregated structure of MWCNT in the polymer matrix is most probable for coincidence of the minimum of  $k$  variation with  $\varphi_c$  value. It is necessary to note that decrease of  $k$  at low filler content was also observed by Moisala et al., 2006 and Grunlan et al., 2006, respectively, for epoxy resin and poly(vinyl acetate) latex filled with SWCNT. These authors explained this phenomenon by the presence of very high interfacial resistance to the heat flow, associated with poor phonon coupling between nanotubes and the polymeric matrix.

Comparison of dependencies of the PVC/MWCNT electrical conductivity  $\sigma$  and thermal conductivity  $k$  against MWCNT concentration demonstrates their different character. Particular feature of electrical conductivity is the presence of a percolation threshold  $\varphi_c$ . Formation of an infinite conductive cluster leads to sharp increase of the conductivity by many orders of magnitude starting from  $\varphi = \varphi_c$ . The thermal conductivity  $k$  exhibits no percolation behaviour. The  $k=f(\varphi)$  is a monotonous function, with the exception of minimum, which was discussed above. The reasons for such a difference were analyzed in (Shenogina et al., 2005), where it was found that large difference between thermal conductivity ratio  $k_f/k_p$  and electrical conductivity ratio  $\sigma_f/\sigma_p$  (where  $k_f$ ,  $\sigma_f$  are conductivities of the filler and  $k_p$ ,  $\sigma_p$  are conductivities of the polymer matrix) might explain this effect. In fact, transport of electrical charges takes place only along the filler phase without contribution of the polymer matrix. Therefore, such transport critically depends on the presence of percolation and formation of the conductive clusters. By contrast, thermal conductivity always involves the polymer matrix in the heat transport. As far as thermal conductivities of the filler and polymer phases are comparable, it leads to insensitivity of the thermal conductivity to formation of the conductive cluster. Besides, the authors (Shenogina et al., 2005) considered the presence of a large interfacial thermal resistance in the filled systems as a one more reason for the lack of percolation in the thermal conductivity behaviour.

Experimental results presented in Fig. 13 show that starting from 0.14 vol. % of MWCNT, the thermal conductivity slowly rises with increase of the filler content. For two-phase systems, the concentration dependence of the thermal conductivity can be described by a large number of equations (Progerlhof et al., 1976). All of them lie within the interval between the largest thermal conductivity  $k_{\parallel}$  (when the system is represented by a parallel set of plates extended in direction of the heat flow):

$$k_{//} = k_f \varphi + k_p (1 - \varphi) \quad (13)$$

to the smallest thermal conductivity  $k_{\perp}$  (when the plates are stacked in series in a plane perpendicular to direction of the heat flow):

$$\frac{1}{k_{\perp}} = \frac{\varphi}{k_f} + \frac{(1 - \varphi)}{k_p} \quad (14)$$

The thermal conductivity of real two-phase systems lies within the interval between functions (13) and (14) and can not be higher than  $k_{//}$  or lower than  $k_{\perp}$ . In our computations, we have taken  $k_p = k$  ( $\varphi = 0.14\%$ ) as the thermal conductivity value of the matrix. Using of eq. (13) for calculation of the concentration dependence of  $k$  for PVC/MWCNT composites gives good agreement with experimental results if we choose  $k_f = 1.07 \text{ Wm}^{-1} \text{ K}^{-1}$ ; however, this value is unacceptable for thermal conductivity of the MWCNT. The values of  $k$  calculated using eq. (14) lie lower than experimental points whatever values of  $k_f$ . Hence, these boundary relations are not suitable for prediction of the value of thermal conductivity  $k_f$  of MWCNT.

Some authors (Nan et al., 2003) have proposed a simple equation for description of  $k = f(\varphi)$  in the case of oil suspension/CNT systems with low content of CNTs ( $\varphi \leq 1\%$ ):

$$k = k_p + \frac{\varphi \cdot k_f}{3} \quad (15)$$

Eq. (15) fits our experimental data quite well if the value of  $k_f$  is equal to  $2.7 \text{ Wm}^{-1} \text{ K}^{-1}$ ; this value is also too low. In ref. (Mamunya et al., 2002b) it has been shown that the Lichtenecker's equation is suitable for description of the thermal conductivity of the filled systems:

$$\log k = (1 - \varphi) \log k_p + \varphi \log k_f \quad (16)$$

The thermal conductivity of PVC/MWCNT composites, calculated according to eq. (16), is plotted in Fig. 13 for several  $k_f$  values. Line 1 was computed using  $k_f = 55 \text{ Wm}^{-1} \text{ K}^{-1}$ . It can be seen that this function is in quite good agreement with experimental data. Such value of the filler conductivity  $k_f$  is lower than the one predicted for carbon nanotubes as  $k_f = 3000 \text{ Wm}^{-1} \text{ K}^{-1}$  for MWCNT and  $6000 \text{ Wm}^{-1} \text{ K}^{-1}$  for SWCNT (Berber et al., 2000), and even lower than the thermal conductivity of bulk graphite  $k_g = 209 \text{ Wm}^{-1} \text{ K}^{-1}$  (Agari et al., 1985, 1987).

Lines 2, 3 and 4 in Fig. 13 represent data calculated according to eq. (14) for  $k_f = 500 \text{ Wm}^{-1} \text{ K}^{-1}$ , used for the oil suspension/CNT systems (Nan et al., 2003; Xue, 2005) and for higher values of  $k_f$  (1000 and  $5000 \text{ Wm}^{-1} \text{ K}^{-1}$ ), which were predicted for carbon nanotubes. In the last three cases, a big divergence between predictions and experimental data is observed. It is necessary to note that experimental measurements were carried out within the range of low concentrations of MWCNT (less than 1 vol.%) and we extrapolated the calculated values to  $\varphi = 100 \text{ vol. } \%$ , in order to predict the value of  $k_f$  so such prediction is rather approximate. Moreover, it was shown in (Huang et al., 2005), that when MWCNT within the polymer matrix are aligned in direction of the heat flow, the thermal conductivity of such a composite is essentially higher than for the system with dispersed MWCNT. The value of

the thermal conductivity of aligned MWCNT array was determined as  $k_f \geq 160 \text{ Wm}^{-1}\text{K}^{-1}$ , which is close to conductivity of the graphite.

## 5. Conclusion

Investigation of electrical conductivity  $\sigma_{DC}$  of the PVC/MWCNT and UHMWPE/MWCNT composites depending on MWCNT content revealed the ultralow values of percolation threshold,  $\varphi_c = 0.00047$  ( $\approx 0.05$  vol. %) and  $\varphi_c = 0.00036$  ( $\approx 0.04$  vol. %), respectively. It is caused by two reasons: high anisotropy of MWCNT with aspect ratio length/diameter  $\sim 1000$  and the presence of segregated structure of MWCNT within polymer matrix with distribution of nanotubes on the boundaries between polymer grains. The geometrical shell structure model predicts the value of percolation threshold which is in excellent agreement with the experimental values.

Frequency dependence of the dielectric parameters  $\varepsilon'$  and conductivity  $\sigma_{AC}$  demonstrates different behavior below and above percolation threshold. Interfacial polarization gives a contribution to the complex dielectric permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$  that is resulted in the increasing of  $\varepsilon'$  with the decreasing of frequency  $\omega$ . Power law dependencies  $\varepsilon' \propto \omega^{-1}$  and  $\sigma \propto \omega^x$  were observed in the range of low frequencies that corresponds to an approach of the intercluster polarization (IP) model. At fixed frequency the values of the dielectric parameters  $\varepsilon'$  and  $\tan \delta$  revealed the percolation behavior with identical value of the percolation threshold to  $\varphi_c$  obtained by measurements of DC conductivity.

The thermal conductivity  $k$  does not reveal any percolation behaviour in the vicinity of electrical percolation concentration  $\varphi = \varphi_c$  but exhibits minimum in this region. This effect can be explained by running of two opposite processes: first, the presence of interfacial resistance to heat flow on the polymer-MWCNT boundary that decreases the values of  $k$ ; and a subsequent increase of the heat flow due to appearance of a noticeable concentration of the filler phase with high thermal conductivity. Lichtenecker's equation allowed to predict the value of the thermal conductivity of MWCNT,  $k_f = 55 \text{ Wm}^{-1}\text{K}^{-1}$ . This value is much lower than the theoretically predicted one for nanotubes  $k_f = 10^3 - 10^4 \text{ Wm}^{-1}\text{K}^{-1}$ . In the polymer materials filled with conductive particles, both polymeric and filler phases always take part in the heat transport. So, the thermal conductivity value of such a system depends on relative concentrations of the polymer and filler.

## 6. Acknowledgment

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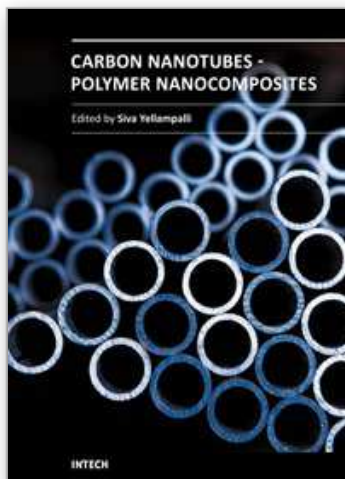
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## **Carbon Nanotubes - Polymer Nanocomposites**

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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This book focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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