Electrical Properties of Carbon Black-filled Polymer Composites

Haralampos Zois[1], Lazaros Apekis[1], Mária Omastová[2]*

[1] National Technical University of Athens, Department of Physics, Zografou Campus, 157 80 Athens, Greece
[2] Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia

Summary: This work deals with the dielectric properties of conductive composite materials, which consist of thermoplastic polypropylene (PP) matrix filled with carbon black (CB). The CB concentration was systematically varied in a wide range. Our main interest is focused on the investigation of electrical conductivity mechanism and related percolation phenomena in these materials. To study the electrical and dielectric properties of composites we used broadband ac dielectric relaxation spectroscopy (DRS) techniques in a wide temperature range. By measurements of complex dielectric permittivity, ε^*, the dependence of ac conductivity, σ_{ac}, and dc conductivity, σ_{dc}, on the frequency, the temperature and the concentration of the conductive filler was investigated. The behavior of this system is described by means of percolation theory. The percolation threshold, P_C, value was calculated to be 6.2 wt. % CB. Both, dielectric constant and dc conductivity follow power-law behavior, yielding values for the critical exponents, which are in good agreement with the theoretical ones. Indications for tunneling effect in the charge carriers transport through the composites are presented. The temperature dependence of dc conductivity gives evidence for the presence of positive temperature coefficient (PTC) effect.

Introduction

The electrical and dielectric properties of composite materials based on conducting additives dispersed within insulating matrices have been the subject of both theoretical and experimental studies over the last decades, due to their wide range of industrial applications[1)]. They can be used, as insulating materials with special properties (dielectric, mechanical, optical, and thermal), or as electrically conductive materials. At the same time, these materials hold general interest from fundamental point of view.

Carbon black- polymer composites have been the subject of extensive research[2,3)], due to their high conductivity value, relatively low price and good ultimate and processing properties.

 CCC 1022-1360/00/$ 17.50+.50/0

These composites are typical representatives of percolative systems. The addition of suitable types and concentrations of filler particles leads to compounds with conductivity varied in a wide range. Detailed investigations in this field contribute to a better understanding of the structure- properties relationship[3-5] at molecular level and, thus, for designing new materials with desirable properties for specific technological applications.

In this work we study the dielectric properties of conductive composite materials, which consist of thermoplastic polypropylene (PP) matrix filled with carbon black (CB). We report our experimental results on the dependence of the dielectric constant and the dc conductivity on the frequency, the temperature and the filler content. Percolation theory[6,7] is used to analyze the experimental results. An effort is made to correlate the temperature dependence of dc conductivity of the systems studied with the positive temperature coefficient (PTC) effect.

Experimental

Materials

Polypropylene (Tatren TF-411, MFI= 10g/10 min., M_W= 210 000 g/mol, M_n= 25 100 g/mol, Slovnaft, Slovak Republic), and carbon black (VULCAN® XC-72R, Cabot Corp., USA) were used as received.

Composite preparation

Composites were prepared by mixing of polypropylene with carbon black in a 50 ml mixing chamber at 75 rpm for 10 min. at 200°C using the Plasti-Corder kneading machine PLE 330 (Brabender, Germany). For the electrical conductivity measurements the prepared composites were compression moulded under 22.5 kN/cm^2 pressure at 200°C for 2 min. into sheets approximately 0.3 mm thick[8]. The exact weight percentage of CB in the composites was determined by means of thermogravimetry using a TG-7 (Perkin-Elmer, USA).

Study of morphology

The microstructure of PP/CB composites was studied by low voltage scanning electron microscopy (SEM) using DSM 982 Gemini (Zeiss Oberkochen, Germany) equipment. Samples without any metal coating were glued to an electrically grounded sample holder using double-faced conductive tape.

Dielectric relaxation spectroscopy measurements

Ac dielectric relaxation spectroscopy (DRS) measurements[9] of the complex dielectric permittivity: $\varepsilon^*=\varepsilon'-i\,\varepsilon''$ were carried out using two different complementary experimental set-ups. In the frequency range of 20-10^6 Hz a Hewlett-Packard precision LCR meter, HP 4192A,

was used. A Schlumberger frequency response analyzer (FRA 1260) supplemented by a buffer amplifier of variable gain (Chelsea dielectric interface) was used for measurements in the frequency region 10^{-1}-10^{6} Hz. The temperature varied between 120 and 420 K. For both set-ups the samples were in form of discs 30 mm in diameter and about 0.3 mm thick. A two-terminal parallel-plate capacitor dielectric cell with aluminium foil or gold metal electrodes (Novocontrol) was used combined with a cryostat and the Quatro Cryosystem (Novocontrol)[10].

Results and Discussion

Figs. 1 and 2 show logarithmic plots of ε' (real part of the complex dielectric permittivity) and σ_{dc} (dc conductivity) as a function of carbon black weight content, P, measured at room temperature. σ_{dc} value means the value of ac conductivity at the lowest frequency of measurement (10^{-1} Hz). An increase of both ε' and σ_{dc} was observed with increasing amount of CB. This increase is sharp at a critical filler content, what corresponds to the so-called percolation threshold, P_C. Near this region the addition of a small CB amount causes a significant conductivity increase (about 8 orders of magnitude). For CB concentration lower than P_C, samples exhibit insulating behavior, while for CB content close to and higher than P_C, samples behave as conductors. Percolation threshold value depends on many factors, such as the size, the shape and the spatial distribution (topology) of the filler particles within the host polymer matrix, the adhesion and the possible interactions between the two phases and, finally, the processing method.

According to the percolation theory[6,7], for conductive filler content higher than P_C, a continuous infinite network of conducting elements, which are in physical contact, has been formed through the polymer matrix. The electrical percolation phenomenon has been thoroughly studied during the last years. Although many experimental works study this phenomenon, no general theory exists, that can satisfactorily describe all experimental results. Several statistical percolation[6,11,12], thermodynamic[13,14] and geometrical[15] models have been proposed. To explain the percolation phenomenon in binary mixtures, several structure-oriented percolation models have also been introduced. A detailed discussion on the latter models can be found in the paper published by Lux[16].

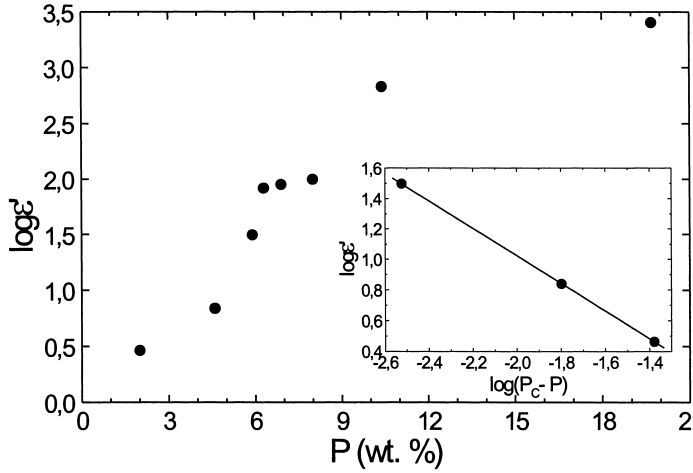

Fig. 1: Dielectric constant (ε′) as a function of CB weight content (P), measured at room temperature. The inset presents plot of logε′ vs. log(P_C-P). The slope of the straight line is: s = 0.90. (P_C - percolation filler concentration)

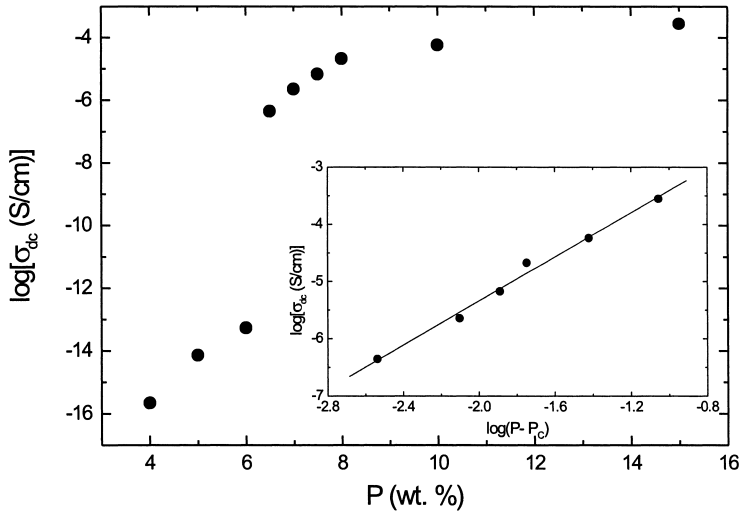

Fig. 2: The dependence of logσ_{dc} on CB concentration (P), measured at room temperature. The inset is the linear plot of logσ_{dc} as a function of log(P-P_C). The straight line has a slope of t = 1.93.

The theoretical approach of Kirkpatrick[6] and Stauffer[7], for the conduction of a conductor-insulator composite, predicts that dielectric constant and dc conductivity should follow, near the threshold, the universal scaling laws:

$$\varepsilon' \propto (P_C - P)^{-s} \text{ , for } P<P_C \qquad (1) \qquad \text{and} \qquad \sigma_{dc} \propto (P - P_C)^{t} \text{ , for } P>P_C \qquad (2)$$

The critical exponents t and s depend only on the dimensionality of the system and not on its geometrical characteristics[6,7]. In particular, for three-dimensional structures, values of t= 1.7-2.0 and s= 0.7-0.9 have been reported[17-19]. For the PP/CB composites studied in this work, the values of s and t have been determined, as shown in the insets of Figs. 1 and 2, by the slope of the least-squares fitting line of each plot. The best fitting gives: P_C= 6.2 wt. % CB, s= 0.901±0.002 and t =1.928±0.094. The critical exponent values are in good agreement with theoretical predictions[20], as well as with other experimental values reported for carbon black filled polymer systems[17-19]. The obtained P_C value is relatively low compared with other types of CB-polymer systems. Low values of P_C are related with highly structured carbon black, due to the large effective volume of CB particles of this kind[4,19]. XC-72 carbon black of the composites studied in this work is considered as a medium-structure carbon black[3,4]. Therefore, relatively low values for P_C should be expected.

Additional information about the morphology of the samples can be obtained from SEM micrographs (Fig. 3). At carbon black concentration 2 wt. % (Fig. 3a) only individual particles of the filler homogeneously distributed within the PP matrix are visible. For CB content above percolation threshold, agglomeration of filler particles is observed and feature of conducting networks created from CB agglomerates is possible to see, as shown in Fig. 3b.

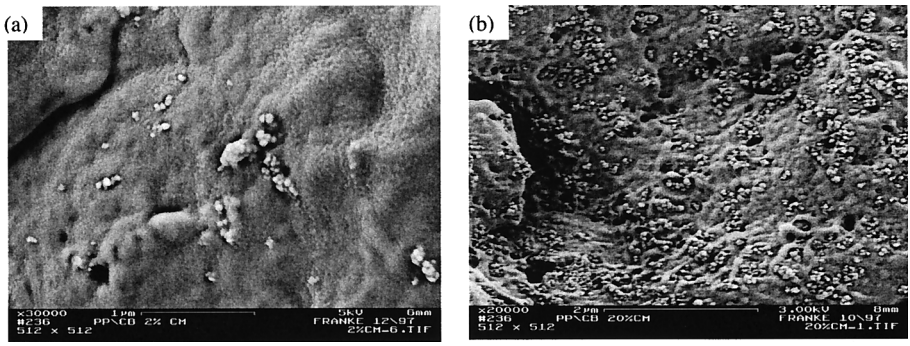

Fig. 3: SEM micrographs of PP/CB composites with CB concentration equal to 2 wt. % (a) and 20 wt. % (b).

Several mechanisms have been proposed to explain the conduction mechanism and the nature of the contacts between conductive clusters in a conductor-insulator composite. In percolation theory, the formation of an infinite percolative network through the compound is assumed to occur via physical contact between the conductive aggregates. In real composite systems the charge carriers are allowed to tunnel from one conductive cluster to another without any physical contact. In carbon black composites tunneling conduction has been reported[2,19]. In these systems, electrical conductivity can be ascribed to tunneling through a potential barrier of varying height, due to thermal fluctuations[2,19]. For a random distribution of the conducting particles, it can be shown that the mean average distance among particles is proportional to $P^{-1/3}$. This means that $\log\sigma_{dc}$ should be proportional to $P^{-1/3}$, too[19]. In Fig. 4, the relation between $\log\sigma_{dc}$ and $P^{-1/3}$ is tested. The linear relation of the plot $\log\sigma_{dc}$ vs. $P^{-1/3}$ is an indication that tunneling conduction may be the main conductivity mechanism of the PP/CB composites studied. Such a mechanism would yield to increased conductivity values before any contact between particles has been achieved[19].

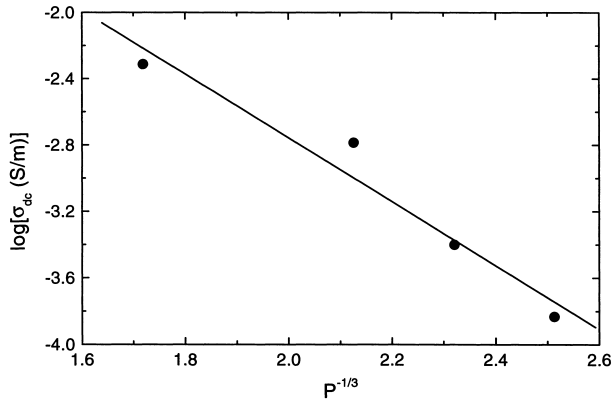

Fig. 4: Plot of log σ_{dc} as a function of filler concentration $P^{-1/3}$.

Fig. 5 presents the temperature dependence of dc conductivity for the composites with CB content above percolation threshold (P higher than P_C). As shown in this Figure, dc conductivity decreases when the temperature approaches the melting point temperature of the polymer matrix (T_m = 165°C). This behavior is related to the positive temperature coefficient (PTC) effect[21,22]. In general, the PTC effect is connected with a large volume expansion of the polymer matrix leading to discontinuities of the conducting network, due to the separation

of the CB conductive aggregates with heating[23,24]. Similar behavior has been reported in other CB filled polymer composites, containing semicrystalline polymer matrix. In such composites, the electrical resistivity changes by several orders of magnitude for a temperature change of only few degrees[21].

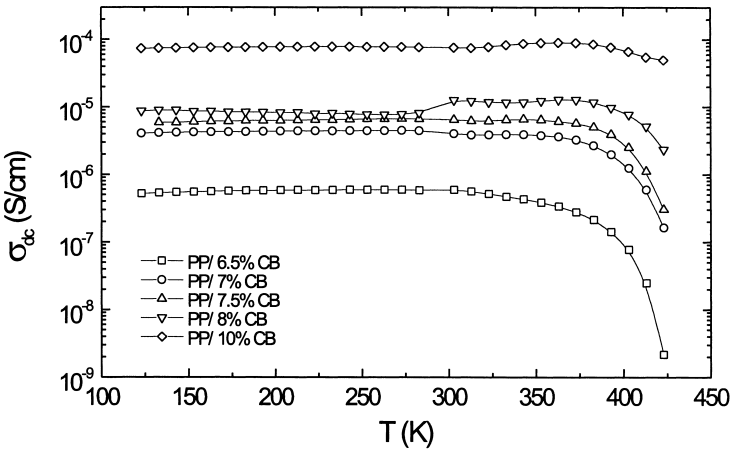

Fig. 5: dc conductivity as a function of temperature for the samples with CB weight content higher than P_C (CB concentrations are shown on the plot).

As shown in Fig. 5, the most pronounced decrease of conductivity, about two orders of magnitude during heating the composites up to 420 K, was found in PP/CB composite containing 6.5 wt. % CB. In the composites with higher CB content, smaller conductivity decrease was measured during heating. The increase of conductive filler content in composite results in a creation of more perfect and temperature resistant conductive filler network, which leads to the increase of viscosity and electrical conductivity of the material[8]. PTC effect in PP/CB composites will be studied in more details in near future by heating the composites to higher temperatures.

Conclusions

The dielectric constant, ε', and dc conductivity, σ_{dc}, of conductive composite materials consisting of thermoplastic polypropylene matrix filled with carbon black have been studied as a function of frequency, temperature and filler content. The general scaling laws predicted

by the percolation theory have been confirmed. The percolation threshold, P_C, was calculated to be 6.2 wt. % CB. We also calculated the critical exponent values, which was found to be in good agreement with the theoretical ones. Indications for tunnelling effect in the charge carriers transport through the composites are presented. Measurements of temperature dependence of dc conductivity give evidence for the presence of positive temperature coefficient (PTC) effect. The sensitivity of composite containing lower CB content to changes of temperature near melting point of PP matrix is higher compare to composites with higher CB content.

Acknowledgement

The research was supported by the Grant Agency for Science of the Slovak Academy of Sciences (GAV-2/1060/21).

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